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PREPARATION AND ANALYSES OF CHEMICALLY SORPTIVE YARNS FROM RAYON AND ACRYLIC PRECURSORS

by

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Georgia Institute Of Technology

Contract No. DAAG 17-76-C-0092

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Research was conducted to develop and demonstrate a continuous process for production of a highly sorptive carbon fiber meeting specific strength and denier requirements. The initial evaluation was on a rayon precursor specified by the contract, Enka Glanzstoff Supreme Cordenka tire cord yarn. A continuous pyrolysis line was assembled that centered around impregnation of the rayon with a carbonization promoter solution followed by staged pyrolysis to a maximum temperature of 1000°C. After numerous unsuccessful trials utilizing a variety of pyrolysis conditions, the Supreme Cordenka was concluded not to be

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a feasible candidate for continuous carbonization. Frequent breaks were attributed to the chemical and physical characteristics of the yarn causing uncontrolled "hot spots".

The research was then directed toward an alternate rayon precursor marketed by Avtex fibers that has been designed and spun specifically for good carbonization characteristics. The yarn exhibited extremely facile pyrolysis behavior, with long continuous runs conducted. Maximum activation attained was 9.5% adsorption by weight of CCl_4 vapor, while maximum yarn properties of 0.39 gpd tenacity/1.8% elongation at break/1200 denier were obtained. The Avtex rayon was thus concluded to possess excellent potential as a sorptive carbon yarn precursor.

A staple acrylic yarn, based on Monsanto's Type P16 fiber, was investigated as an alternate precursor to rayon in continuous carbonization to a sorptive yarn. A semicontinuous process, based on two separate continuous phases operated at different yarn speeds, was developed to pyrolyze the yarn. The first stage involved impregnation with sodium glyceroxide to form nitrile cyclization promoter sites, while the second stage consisted of careful pre-oxidation followed by rapid carbonization. Staple, flexible carbon yarn was produced by the process that exhibited good qualitative properties.

SUMMARY

Research was conducted under Natick Contract Number DAAG17-76-C-0092 to develop and demonstrate a continuous process for production of a highly sorptive carbon fiber meeting specific strength and denier requirements. The initial evaluation was on a rayon precursor specified by the contract, Enka Glanzstoff Supreme Cordenka tire cord yarn. A continuous pyrolysis line was assembled that centered around impregnation of the rayon with a carbonization promoter solution consisting of concentrated monosodium phosphate/boric acid in water, followed by staged pyrolysis to a maximum temperature of 1000°C.

After numerous unsuccessful trials utilizing a variety of pyrolysis conditions, the Investigator concluded that the Supreme Cordenka was not a feasible candidate for continuous carbonization. The frequent breaks encountered at temperatures greater than 700°C with the Supreme Cordenka were attributed to the chemical and physical characteristics of the yarn causing uncontrolled "hot spots". These characteristics were introduced in the development and spinning of the filament yarn to impart optimum performance in vehicle tires.

The research was then directed toward an alternate rayon precursor marketed by Avtex fibers that had been designed and spun specifically for good carbonization characteristics. The yarn exhibited extremely facile pyrolysis behavior with continuous runs of sufficient length conducted to adequately demonstrate the feasibility of the carbonization process. Optimization of the properties of the Avtex precursor-based carbon fibers was limited due to the level of funds remaining on the contract after the Enka rayon trials. Maximum activation attained was 9.5% adsorption by weight of CCl_4 vapor, while maximum yarn properties of 0.39 gpd tenacity/1.8% elongation at break/1200 denier were obtained. The Avtex rayon was thus concluded to possess excellent potential as a sorptive carbon yarn precursor. Further research will be necessary, however, to fully reach the carbon yarn's capabilities.

Static tests were also conducted on the Supreme Cordenka yarn to screen alternate carbonization promoters. The batch pyrolysis was initially directed

toward two Monsanto flame-retardant formulations, MCC-100 and MCC-300, based on a proprietary phosphoramide. The formulations were selected for study due to their ability to give high char:volatiles ratios with cellulosics. Pyrolysis behavior on the static system with the Enka rayon was poor, however, with frequent breaks occurring below 500°C. Attempts to obtain a research-stage phosphoramide formulation from the Exxon Company were unsuccessful due to low supply. Lowering the strength of the NaH_2PO_4/H_3BO_3 formulation from the continuous line did not result in improved pyrolysis behavior on the batch process with the Enka yarn. No trials on the batch system were conducted with the Avtex precursor.

A staple acrylic yarn, based on Monsanto's Type P16 fiber, was subjected to preliminary investigation as an alternate precursor to rayon in continuous carbonization to a sorptive yarn. A semicontinuous process, based on two separate continuous phases operated at different yarn speeds, was developed to pyrolyze the yarn. The first stage involved impregnation with sodium glyceroxide in glycerine to form nitrile cyclization promoter sites, while the second stage consisted of careful preoxidation followed by rapid carbonization. Staple flexible carbon yarn was produced by the process that exhibited good qualitative properties. No quantitative properties were determined, however, due to termination of the project.

PREFACE

For several years the U.S. Army Natick Research and Development Command has been seriously considering the preparation of activated carbon yarns for potential use in protective clothing. After showing that the concept had potential in the early stages, several pounds of yarn were purchased from Union Carbide Corporation and the 3M Company. The 3M yarn proved to be the most sorptive and useful. These yarns were woven and knit into various fabric constructions and the best of these fabrics were made in a quantity large enough to fabricate prototype garments which are currently being evaluated for durability and comfort. Soon after purchase of the 3M yarn, the 3M Company dismantled its production line and decided not to make further quantities, partly because the specific rayon precursor yarn was no longer available. This work showed that activated carbon yarn could be used to make protective clothing and that further development of fabrics and garments was warranted. Therefore, a new source of activated carbon yarn was needed. The contract effort reported here describes the first attempts to develop a new activated carbon yarn similar to that of the 3M Company. The ready availability and high-volume production of commercially - available rayon tire cord yarns dictated that the initial research be directed toward this type precursor. American Enka's Glanzstoff Supreme Cordenka tire cord yarn was selected as the initial "precursor" candidate. The Georgia Institute of Technology undertook the effort and used some of the Institute's funds to purchase and install equipment and study materials not specifically called for in the contract. This was done becuase the Institute was building up their capabilities in the carbon products area. The principal Investigator for the Georgia Institute of Technology was Dr. Fred L. Cook. The Project Officer and Contract Officer's Representative for the U.S. Army Natick Research and Development Command was Dr. Richard N. MacNair.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

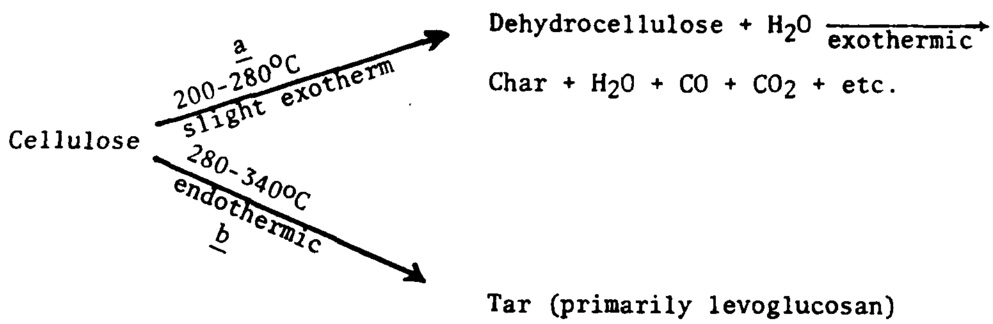
LIST OF TABLES

PREPARATION AND ANALYSES OF CHEMICALLY SORPTIVE
YARNS FROM RAYON AND ACRYLIC PRECURSORS

INTRODUCTION

Rayon Precursors

Considerable research has been conducted on the thermal degradation of rayon, both from a flame retardant viewpoint and a carbon/graphite fiber viewpoint. The accepted general degradation pattern for cellulose is as follows:[1]



Specifically, the degradation steps are as follows:[1]

1. A dehydration, first observed at 220°C in the presence of a flame retardant.
2. A depolymerization, with product volatilization, evident at about 280°C.
3. A decomposition of the dehydrocellulose formed in path a into a number of gaseous products and residual tar.

Schwenker and Beck discovered by gas chromatography of the volatiles produced by cellulose pyrolysis in nitrogen or air that the same products were formed irrespective of the pyrolysis atmosphere.[2] The conclusion

was that the degradation mechanism was nonoxidative in nature, a theory that has been embraced by other investigators.[3]

The role of flame retardants is the same in fire prevention and carbon fiber production: to catalyze the char-forming reactions (path a) at the expense of the depolymerization/tarring reactions (path b). The flame retardants promote the dehydration of the cellulose at low temperatures (150°-200°C) and stabilize the molecule.[4] Carbonization promotion is also effected through increased reaction rates, reaction spread over a wider temperature range, and improved carbonization yield.

The mechanisms of degradation of cellulose in the absence and presence of nitrogen- and phosphorus-containing carbonization promoters have been reviewed extensively in the literature.[1,5,6] Either Lewis acids or bases can effect the dehydration and decomposition of cellulose.

In the engineering area, the conversion of rayon into high-performance carbon or graphite fibers for reinforcement of resin matrices has dominated research over the past twenty years.[4] Three basic steps are involved in the conversion: heat treatment, carbonization, and graphitization. Stress is normally applied during the graphitization step to achieve high-modulus fibers. Structurally, graphite fibers from rayon exhibit graphite c axes preferentially confined to the plane tranverse to the fiber axis, resulting in anisotropic mechanical properties.[4]

The patent literature is extensive in production methods for producing high performance graphite fibers (HPGF) from rayon.[5-11] However, little information has been published on production of carbon fibers that possess high sorptivity characteristics. Peters and coworkers have patented the most definitive research in production of sorptive carbon fibers from rayon.[12,13] The initial patent detailed various nitrogeneous salts, which, when utilized with boric acid, acted as carbonization promoters to yield flexible, strong carbon fibers.[4] A typical example of impregnation chemicals consisted of:[12]

	Parts by Weight
Ammonium sulfamate	10
Dibasic ammonium phosphate	4
Dicyandiamide	2
Boric acid	4
Water	80

A later patent, however, revealed more efficient results with four monobasic salts and boric acid, and in particular monosodium phosphate/boric acid combinations.[13] Sorptive yarn was produced continuously utilizing the following chemical impregnation bath:

Chemical	Concentration (weight percent)
Monosodium phosphate	20
Boric acid	4

The pull-rate of the yarn through the reported system was 12 inches/minute. The conductive carbon yarn had a tenacity of 2.6 gpd, a denier of 775, and a carbon weight percent of 82.3 under the utilized oven conditions. Conversion at a temperature profile of 232°C/277°C/1427°C gave a carbonized yarn with a 3.0 gpd tenacity and 835 denier. Analysis of the carbonized yarns revealed the following:[13]

Element	Weight Percent
Carbon	82.3
Hydrogen	0.8
Nitrogen	4.4
Boron	2.5
Sodium	nil

Several key factors were apparent from the Peters patents:

1. Both boron and nitrogen were absorbed into the fiber structure, resulting in a several-fold increase in breaking strength.
2. The rayon yarn used in the continuous process was described as a 3.5 Z-twist yarn of 1650 denier continuous filament. The yarn required <u>no scouring</u>, which indicated that the yarn was not an "off-the-shelf" tire cord. The latter always contain excessive amine-based spin finishes and zinc salts that require strenuous scouring for partial removal. The yarn was thus likely a specialty yarn that had been specifically designed for facile carbonization, similar to the Avtex precursor discussed later in this report.

3. The salt bath was hot during impregnation to facilitate complete diffusion of the carbonization promoter solution to the center of the fiber. No specific impregnation temperature was given, though the term "near boil" was referred to in the patent. Deionized water was specified as the preferred solvent.
4. A pickup of salt solids (dry basis by weight) of about 10-30% was preferred, attained by removal of excess solution after impregnation to give a 100% wet pickup of salt solution.
5. Despite the absence of effect of oxygen on degradation by gas chromatography,[2] the 3M researchers found that oxygen appeared to be essential to the production of carbon fibers with the desired properties. A mixture of air with inert diluent was necessary, however, to reduce the weight percent of oxygen to around 5% and to prevent uncontrolled exotherms during pyrolysis.
6. Nitrogen was entered into the ovens counter-currently to the yarn flow direction. The counter-flow technique was claimed to aid in exotherm control and render a product of maximum tenacity.
7. A straight-flow process was utilized, with the yarn kept under minimum tension throughout the system. The resulting yarns were stated to be predominately amorphous by X-ray diffraction.
8. The carbon product, after cooling was claimed to be washable to remove soluble materials detrimental to be desired properties. These materials presumably consisted of the precipitated or sublimed carbonization promoters and/or their degradation products. The washed and dried product had a weight of 60-67% of the original rayon. Washing was not mentioned, however, in the patent example detailing the continuous yarn process, indicating that a continuous washer section was not inserted into the line.

9. Sorptive characteristics were not extensively discussed in the patent. The fibers were determined to be microporous and hygroscopic, as illustrated by adsorption of 20% by weight of water when exposed to an atmosphere of 100% relative humidity and 72°F.

Two critical factors were excluded from the 3M patents. First, the exact nature of the yarn utilized in the continuous yarn experiments was not revealed. Second, the exact gas composition and flow in the critical stabilization oven was not detailed. These two parameters were found to be decisive in developing a continuous pyrolysis line in the research reported herein.

Another key element that was excluded from the patents was a description of the activation process used to obtain the high adsorptivity exhibited by the rayon-based carbon fiber later supplied to the Natick Laboratories. From other literature, CO_2, diluted O_2, steam, and HCl atmospheres have all been utilized to activate carbon fiber in the 1000°C pyrolysis range.[14] None of these oxidizing atmospheres were utilized in the high-temperature oven of the patented process.

Several additional patents have recently addressed the problem of producing sorptive rayon-based carbon fibers. Fukuda et al. impregnated fine rayon yarns (5 denier) with a 10% aqueous solution of phosphoric acid, and heat-treated the dried yarn in an atmosphere derived from propane combustion composed of 80% N_2, 5% CO, 10% CO_2, 2% O_2, and 3% H_2O at a temperature (time) profile of 270°C (5 min. rise)/270°C (30 min.). Activation in the same atmosphere enriched with 30 vol.% water vapor at 850°C (30 min.) gave a fiber with iodine and benzene adsorption capacities of 1000 and 200 mg/g, respectively.[14] Ishizaki et al. used a mixture of 115 parts 85% phosphoric acid and 60 parts urea to generate a condensation product as a rayon carbonization promoter. A temperature profile of 250°C (15 min.)/800°C (50 vol. % steam/50 vol.% N_2) gave a fiber consisting of 90 weight percent carbon with tensile strength of 5 ton/cm^2.[15] Khan et al. desized viscose yarn in boiling ethanol, and impregnated the material in a 1000 ml aqueous solution containing 2 g ammonium sulfamate, 2 g borax, and 30 ml of 75% phosphoric acid. The yarns were predried (500°-550°F (2 min.)), postdried (550°-600°F(2 min., 5 g/end tension)), precarbonized (650°-700°F(2 min.,

5 g/end tension, N_2)) and carbonized (700°-750°F (2 min., 170 g/end tension, N_2)). The flexible product had a high tenacity of 3.44 g/denier and a carbon content of greater than 96%.[16]

The reported research dealt initially with development of a continuous process for carbonizing a specific rayon precursor, an off-the-shelf tire cord yarn produced by Enka Glanzstoff and titled "Supreme Cordenka", and testing of the product's sorptive properties. For reasons detailed herein, however, continuous carbonization of this particular yarn proved unfeasible. The research was then directed toward an alternate rayon precursor marketed by Avtex Fibers, Inc. which was specifically designed for good carbonization characteristics instead of optimum tire cord performance.

Acrylic Precursors

Natick RFP Number DAAG17-76-R-0033 and Contract Number DAAG17-76-C-0092 specified that the prime objective of the reported project was to develop a continuous process for pyrolyzing a new rayon precursor, Enka Glanzstoff Supreme Cordenka viscose tire cord yarn, to highly sorptive carbon fibers that met specific mechanical and denier requirements. Although rayon had been tested successfully as a precursor for sorptive carbon textiles,[12,13] the projected future of regenerated cellulosic fibers is not conducive to long-term reliance on the regenerated cellulosic as a precursor. Several factors have and continue to contribute to the decline in the U. S. production of rayon, including zinc pollution inherent in the process, high energy requirements per pound of fiber, and public acceptance of synthetic fiber substitutes for cellulosics (especially in the tire cord market). Possible replacements for rayon as sorptive carbon fiber precursors are the acrylic fibers, defined as possessing greater than 85% of acrylonitrile repeat units in the polymeric chains.

The acrylics are produced in large quantities by a number of major manufacturers in the U. S. (du Pont, Monsanto, American Cyanamid), and are processed into yarns (usually from staple fibers) suitable for both fabric and carpet applications. Continuous-filament acrylic yarns have traditionally been pyrolyzed in a three-phase process (preoxidation, carbonization, graphitization) to high-tenacity, high-modulus graphite fibers that are utilized in engineering applications.[17] The preoxidation step is necessary to avoid excessive fragmentation in the later high-temperature graphitization, to

stabilize the acrylic by promoting cyclization of the nitrile groups, to crosslink the structure, and to form ionic functional groups, all resulting in a "thermoset" material.[18] Acrylic preoxidized by early workers (200°C, air, 16 hours) exhibited a surprising 57% retention of tenacity (the so-called "black Orlon").[19] Problems connected with the preoxidation of the acrylic fibers (mainly due to uncontrolled exotherms and time-consuming, costly processing) have been eliminated by pretreatment of the yarns with various chemicals prior to preoxidation. The chemical treatments are designed to partially polymerize the nitriles of the parent structure and to introduce reactive initiating groups into the polymer. Both actions facilitate formation of a ladder structure during preoxidation without uncontrollable exothermicity, the latter caused by catastrophic nitrile cyclization. Grassie has shown that various additives to acrylic fibers (selected acidic and basic organic compounds and inorganic salts) broaden the characteristic exotherm revealed by differential thermal analysis on preoxidation with much-reduced differential temperatures. The additives also accelerate the stabilization process.[20] Other pretreatments of acrylic fibers to facilitate the preoxidation to partially carbonized yarns are prominent in the patent literature.[21-23] All of the pretreated yarns showed more rapid, more controllable preoxidation than that exhibited by the untreated acrylics.

As stated, the majority of acrylic yarns utilized commercially for preparation of high-strength, high-modulus carbon fibers are continuous filament in nature. However, the mass-produced acrylic yarns in this country are composed of staple fibers. For utilization of carbonized acrylic fibers for preparation of chemically-sorptive fabrics, where super-strength fibers are not required, staple yarns with appropriate twist in the precursor should suffice. As an added incentive, the cost of continuous carbon fiber is typically 2-3 times that predicted for staple carbon fiber.[24] Johnson has demonstrated that fabric can be woven from oxidized acrylic tow on conventional textile equipment.[25] The oxidized fiber, which retained approximately 37% of its original tensile strength when oxidized without chemical pretreatment (220°C,5 hours), handled well with a suitable size necessary to eliminate abrasion and snagging on weaving the untwisted yarns. The water sorptive characteristics of the preoxidized acrylic fiber have been investigated by Van Hornuff,[26] and the ability of the preoxidized material to absorb organic chemicals is demonstrated by its function as an effective chemical catalyst,

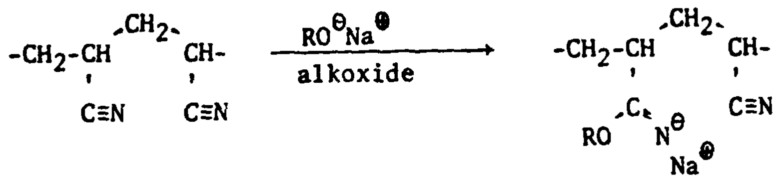
e.g., in the dehydration of alcohols.[27]

A survey of the literature revealed little research on carbonization of staple acrylic yarns nor on sorptive activation of acrylic-based carbon fibers. Conversation with Great Lakes Carbon Company revealed that a HPGF material based on staple acrylic precursors has been marketed, but has met little commercial success. Yamura and Yamane heated a filament, 92:8 acrylonitrile-methyl acrylate copolymer, in air without tension to 250°C in one hour followed by a hold cycle at 250°C for four hours. The fibers were then heated without tension in a 50/50 volume of steam/N_2 to 900°C at a rate of 60°C/minute and held 60 minutes to give activated carbon fibers having surface area of 2100 m^2/g and C_6H_6 absorption of 59% by weight, compared with 730 m^2/g and 11% benzene absorption for fibers prepared in the same manner but under 0.2 mg/denier tension.[28]

Thorne and Price have systematically investigated oxidation of filament polyacrylonitrile-based carbon fibers with CO_2.[29] A carbonized yarn prepared at 1253°K was subjected to CO_2 oxidation in the 960-1320°K range using a dynamic flow system. Reaction rates initially increased with a weight loss of 1.5%, followed by steady-state conditions at weight losses up to 8.7%. Surface topography and gas adsorption studies showed surface smoothing accompanied by localized attack and micropore formation. Apparent surface area (by krypton adsorption) increased from 0.52 m^2/g to 18.2 m^2/g on CO_2 treatment. This activation was considerably lower than that of the rayon-based Pluton B-1 material reported by Arons and Macnair, however (250 m^2/g).[30]

A unique method of facilitating the conversion of continuous filament acrylic yarns to graphite fibers has been recently patented by Monsanto.[31] The fibers were treated in a solution of sodium glyceroxide in glycerine at 195°C (4 minutes), followed by washing, drying, and air oxidation under tension at 270°-312°C for 2.5 hours. The heat-stabilized fiber could then be graphitized directly at 2700°C in one minute under inert atmosphere and 450-500 gpf tension to produce high-strength/high-modulus graphite fibers.

The process appeared to be a semi-continuous operation from the patent examples, with chemical impregnation, washing, and drying being followed by separate air oxidation and graphitization steps. The claim was made, however, that at least the chemical impregnation step could be performed continuously. The glyceroxide apparently acted to form imine anions in the polyacrylonitrile without premature polymerization, the latter termed detrimental to good final product characteristics:



Acrylic Precursor **Imine Anion Initiator**

By chemically facilitating the nitrile polymerization during preoxidation, a highly-crosslinked, naphthyridine-type ladder polymer was formed that could be directly and rapidly converted to the fused benzenoid structure of graphite without slow thermal stage-up.[31]

Based on the paucity of literature references on activated carbon fibers produced from acrylics, the author proposed to investigate the pyrolysis of commercially-available staple acrylic precursors as an alternative to rayon. As a starting point, adaptation of the Monsanto approach[31] to continuous precyclization/carbonization of various staple acrylic yarns was selected. Although only the rayon precursor was specified in this contract, preliminary research on a staple acrylic yarn is contained in this report.

RESEARCH OBJECTIVES

Specific objectives of the reported research, in accordance with specifications in Natick Contract Number DAAG17-76-C-0092, were as follows:

1. Investigate a new rayon precursor, Enka Glanzstoff Supreme Cordenka viscose tire cord yarn, as a potential candidate for continuous production of a highly sorptive (80% by weight sorption of saturated CCl_4 vapor) carbonized yarn possessing specific mechanical and weight properties. The mechanical and weight properties reported for the Supreme Cordenka Yarn in the contract, those obtained in Georgia Tech tests, and the properties desired of the carbonized product are contained in Table 1.
2. Thoroughly test the derived rayon-based carbon fibers for CCl_4 sorptivity and mechanical/textile properties.
3. Without charge to the project, the Investigator entered as an additional objective scouting of new carbonization promoters for the rayon on a batch basis to avoid earlier patent claims in the rayon carbonization area.
4. As additional effort not contained in the contract, the final objective was to investigate commercially-available, staple acrylic yarn as a sorptive carbon fiber precursor.

TABLE 1. PROPERTIES OF THE ENKA RAYON PRECURSOR AND DESIRED PROPERTIES IN CARBONIZED PRODUCT

Information Source	Yarn	Denier	Fil/yarn	Plies	Twist (TPI)	Tenacity (gpd)	Elongation	Initial Modulus (gpd)
Natick Contract DAAG17-76-C-009	Supreme[a] Cordenka	1650	1000	2	1.3Z	5.1	13%	-
Natick Contract DAAG17-76-C-009	Carbonized Product	1000	1000	2	2.5S	2.7	-	-
Georgia Tech	Supreme Cordenka	1613	1000	1[b]	1.3Z	5.0	-	1206

[a] Price of $0.94/lb., quote by Mr. William Dorst, American Enka, Telephone (704)667-7667 (1978).

[b] The Investigator discovered that the yarn was single-ply upon receipt at Georgia Tech.

EXPERIMENTAL

Apparatus, Yarns and Chemicals

Rayon Precursor

The carbonization promoter impregnation bath for all of the rayon trials consisted of a mixed monosodium phosphate (Fisher Scientific) and boric acid (Fisher Scientific) solution. The concentrations were patterned after those of Dickson and Peters,[13] who had reported optimum results with 20% monosodium phosphate and 4% boric acid. Actual concentrations used herein were 16.8% and 3.4%, respectively. Since no basis for the percentage was given in the patent, the assumption was made that the units were in percent weight of solute per weight of solution (% w/w). The calculations used to derive the gram weights necessary to prepare 10ℓ of the impregnation bath at the utilized concentrations are contained in Appendix A. The perchloroethylene and ethanol for prescouring were also obtained from Fisher.

The flow diagram for the optimum rayon pyrolysis line is detailed in Figure 1. The 22-inch simple tube furnaces and direct-readout pyrometers were obtained from Fisher Scientific Company. The Lindberg furnace with controller was obtained through Fisher Scientific. The tubes for the ovens were produced from water-free quartz by Georgia Tech glassblowers. Designs for the tubes in the two types of ovens are given in Figures 2 and 3. Windup was accomplished with a Leesona one-package lab winder fitted with a variable-speed motor with reducer capable of producing the low winding speeds necessary for the process. Air pumps were simple aquarium pumps purchased from Sears Roebuck and Company. Dry nitrogen and carbon dioxide (where applicable) were monitored from tanks by Linde regulators that contained built-in flow meters. Roller and tensioning guides were manufactured by Heinie Corporation. The carbonization promoter bath and the solvent prescour baths were held in stainless steel troughs, while a 3ℓ stainless steel beaker was used as a water wash bath container situated after the impregnation bath.

The rayon yarns utilized were of two types. The properties of the Enka Glanzstoff Supreme Cordenka, specified in the contract, are contained in Table 1. The properties of the alternate rayon precursor investigated, manufactured by Avtex Fibers, are included in Table 2.

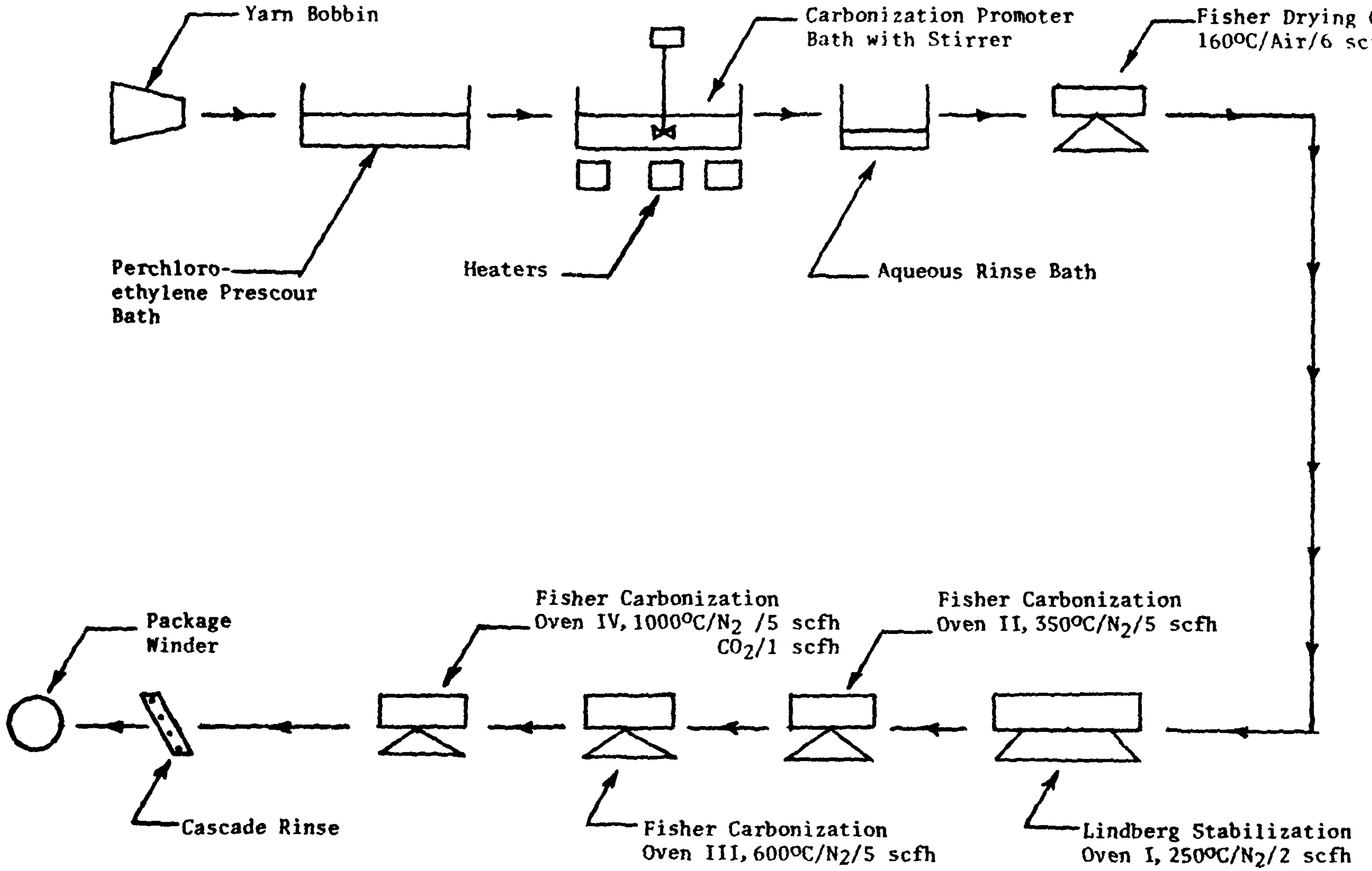


FIGURE 1. Schematic of the Continuous Rayon Pyrolysis Line

Conditions based on Run 76, Appendix D.

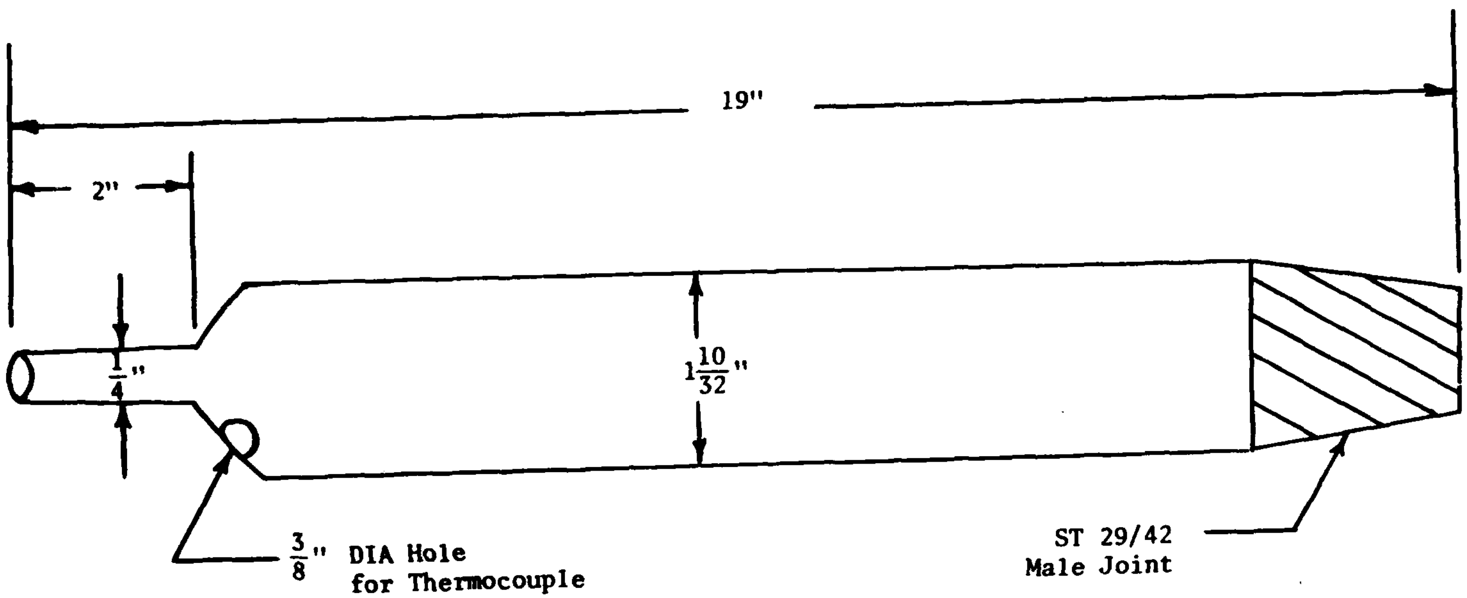


FIGURE 2. Quartz Tube Design Utilized for the Simple Furnaces

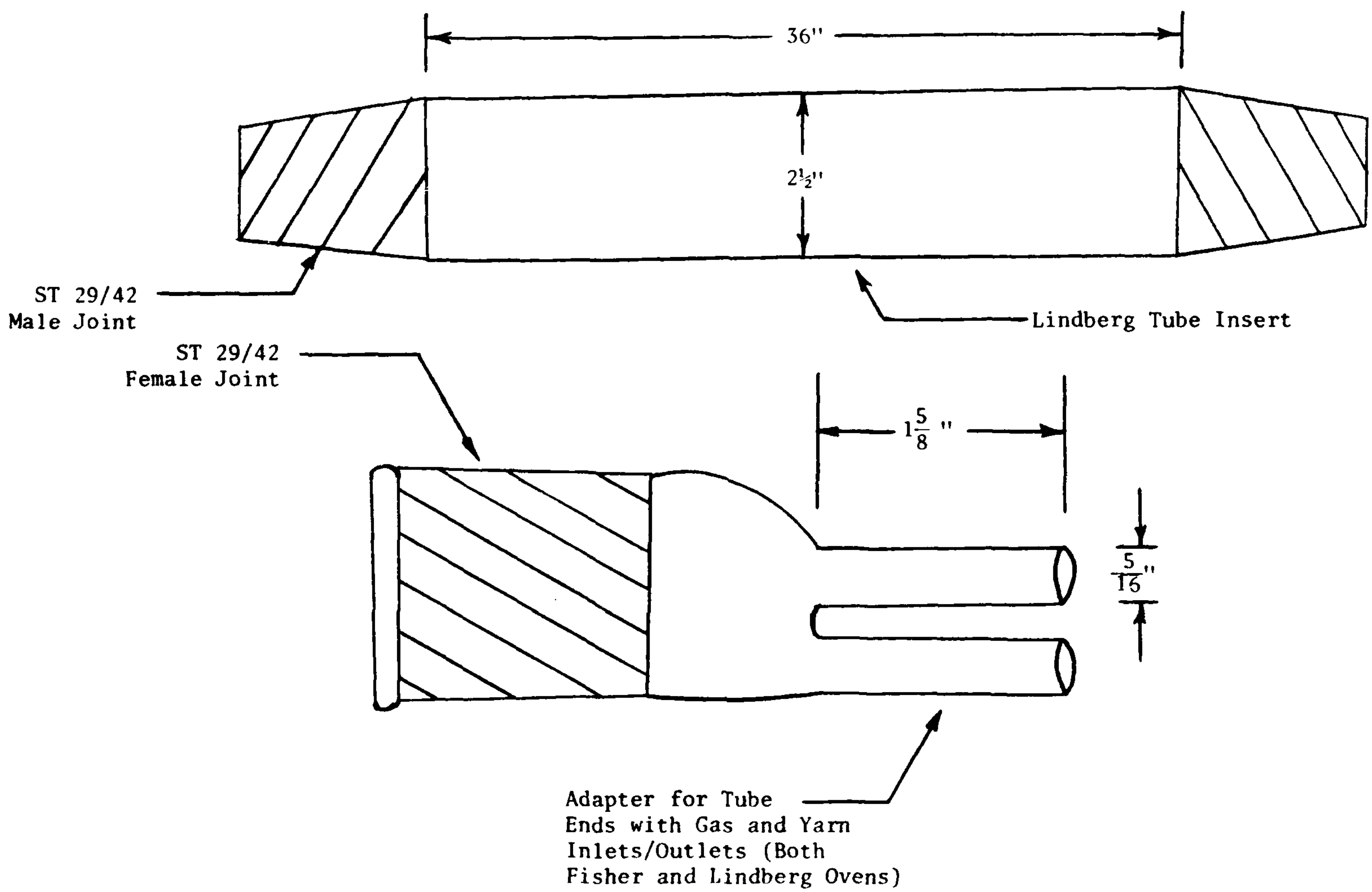


FIGURE 3. Quartz Tube Design Utilized for the Lindberg Sola SIC Oven

TABLE 2. PROPERTIES OF AVTEX RAYON PRECURSOR

Property	Company Value	Ga. Tech Value
Denier	1650	1650
Filament/yarn	720	720
Twist	2.0 Z	2.0 Z
Breaking Strength (gpd)	--	3.1
Breaking Elongation (%)	--	11.5

Static Tests on Rayon Precursor

A static pyrolysis unit consisting of a simple split-tube furnace approximately 12 inches in length with quartz tube and pyrometer was devised to evaluate various new carbonization promoters for rayon.

Discussions with flammability experts and perusal of the literature identified two Monsanto products, MCC-100 and MCC-300, as attractive candidates for new carbonization promoters in the static tests. Communication with Monsanto confirmed that the formulations were based on a phosphoramide (probably trimethylol), and that the MCC 100 was in a concentration of 70% w/w and MCC 300 in a concentration of 35% w/w. The MCC 300 contained a proprietary catalyst that could not be revealed. The flame retardant formulations fit the desired criteria of giving high char:volatiles ratios with cellulosics. Several trials were also run utilizing altered chemical concentrations and conditions than those reported by Peters[13] on the static unit. Static air and dry nitrogen monitored from tanks by Linde regulators that contained built-in flow meters were the atmospheres utilized in the static tests. All of the static tests with rayon were conducted on the Enka Supreme Cordenka tire cord yarn specified in the contract and whose properties are detailed in Table 1.

Sorptivity Tests

Each of the sorptive tests was conducted once on a charcoal sample of undetermined origin as a check on the procedure. The charcoal

was exposed to carbon tetrachloride vapor in a dessicator for 24 hours, weighing both before and after exposure to establish the weight increase. The specific surface area of the charcoal was also measured by low temperature gas adsorption, i.e., the BET technique. Apparently satisfactory results were obtained in both cases, with a weight increase registered due to vapor adsorption and the expected linear BET equation plot being compiled.

CCl_4-sorptive tests were conducted under standard conditions on the carbonized yarns. The individual yarns were placed in a glass jar and the assembly dried for 5.5 hours at 130°C in an oven. The system was then weighed to five decimal places and mounted in a desiccator containing saturated CCl_4 vapor. The system was suctioned off briefly to remove water vapor and air, and the fiber allowed to sit overnight (18 hours) in the CCl_4 environment. The assembly was then removed and weighed immediately to determine CCl_4 adsorption.

Acrylic Precursor

The impregnation bath for the acrylic yarns was patterned after that reported by Menikheim,[31] and consisted of sodium glyceroxide in glycerine at a concentration of 0.02-0.04 meq/g of solution (3.03-6.06 g/ℓ of added sodium hydroxide). The calculations used to derive the yarn weights necessary to prepare 1ℓ of the impregnation bath are contained in Appendix B. The glycerine and sodium hydroxide used in the impregnation bath, as well as the perchloroethylene used in the prescour bath, were all obtained from Fisher Scientific Company.

The flow diagram for the acrylic pyrolysis line is detailed in Figure 4. The drying furnace was a simple tube-type, while the carbonization oven was a Lindberg Sola Basic SIC with controller (Fisher Scientific). The 18-foot tube furnace was constructed in-house, and consisted of three 6-foot sections of 2-inch DIA pyrex tubing with interlocking ground glass joints and capped with adaptors containing yarn and gas flow connections (Figure 3). The glass tubing was wrapped with Nichrome wire, which was in turn connected to three Variacs as power suppliers. The wire was wrapped on the tubes in such a way as to give a temperature gradient of from 200-225°C at the tube entrance to 300-350°C at the tube exit. The wired tube was then wrapped in asbestos tape, and inserted in a 3-inch DIA glass

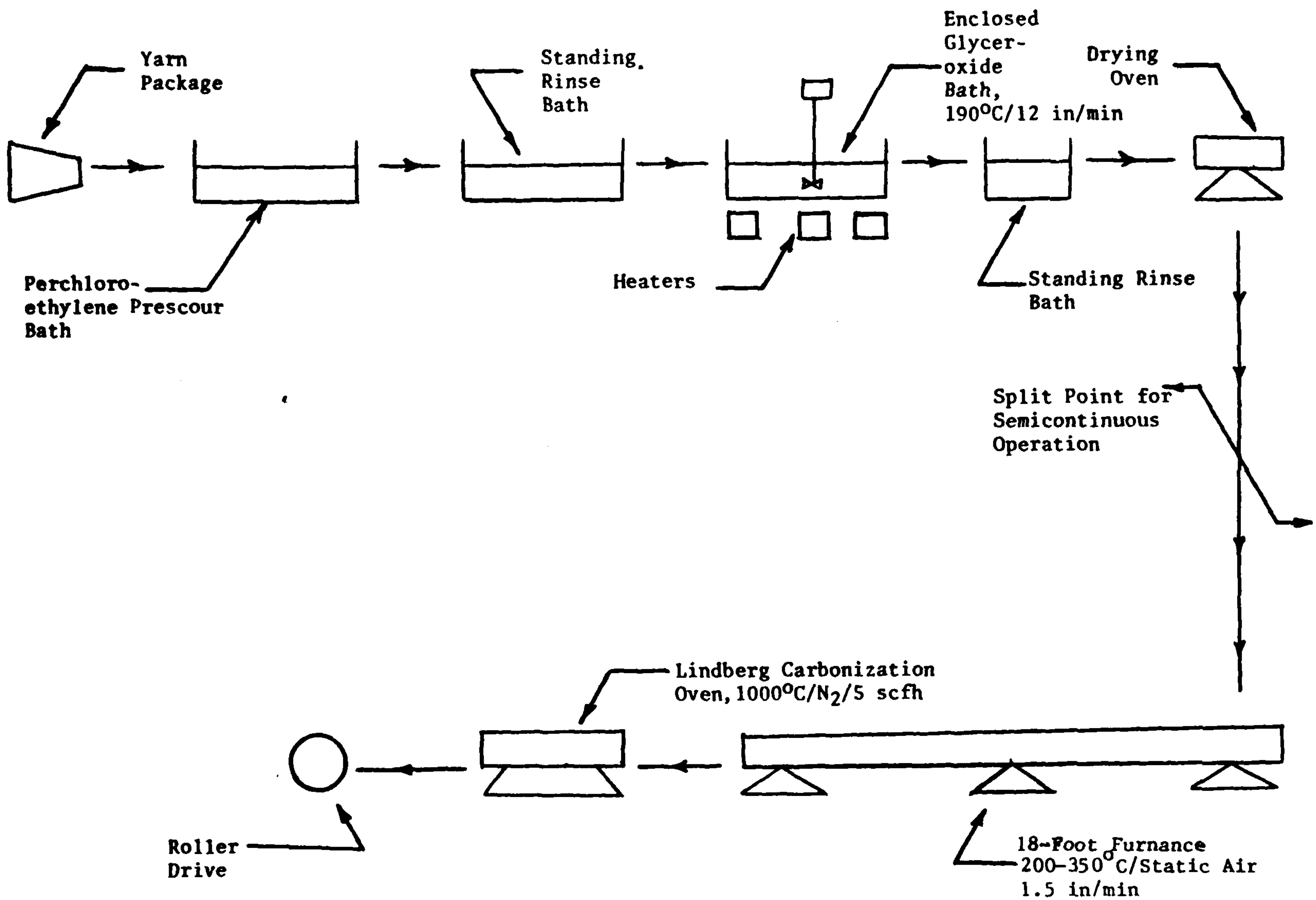


FIGURE 4. Schematic of the Staple Acrylic Pyrolysis Line

sleeve for added insulation and protection. Thermocouples were inserted into the inner tube at nine points along the 18-foot length to monitor the temperature gradient, and the entire tube system was then wrapped in foil-backed fiberglass insulation (3 inches) to reduce radiation/convection losses. Mounts for the furnace were rubber-coated U-clamps normally utilized for securing Dewar flasks. The carbonization Lindberg furnace was assembled the same as described for the rayon pyrolysis line, containing a water-free quartz insert (see Figure 3). The temperature readout for the drying oven was a direct-read Fisher pyrometer, whereas the nine thermocouples from the 18-foot furnace were wired into a switching mechanism connected to a calibrated galvonometer. The system allowed selective temperature readings at any point along the furnace.

Air was supplied to the drying oven by a simple aquarium pump (Sears Roebuck and Company), while static air was utilized in the 18-foot furnace. Dry nitrogen was monitored from tanks by Linde regulators that contained built-in flow meters to the Lindberg carbonization oven.

The bath containers were of stainless steel construction for the glycerine and perchloroethylene dips, while the water washes were held in polyolefin plastic tubs. All of the containers were capable of holding at least ten gallons. Roller guides were purchased from the Heinie Company. The hood over the glyceroxide bath was constructed from plywood and Lexan, with a small electric motor and home clothes dryer flexible tubing used for the exhaust system.

Yarn was propelled through the system by a small Servo motor unit situated after the Lindberg oven that allowed passage of the yarn between two rubber sleeve tracks. The Servo motor was utilized due to the extremely slow speeds that could be attained, much slower than allowed by any of the winder motors available in the School of Textile Engineering. No attempt was made to wind the yarn onto a package during the initial research; instead, it was allowed to freely collect under the Servo motor apparatus.

Three Monsanto staple acrylic yarns were obtained for screening tests as carbon fiber precursors. The only one utilized in the reported research was Monsanto 100% Type 16 Acrilan acrylic yarn. The measured properties of all three staple acrylic yarns are given in Table 3. Additional properties and facts concerning the Type 16 yarn are contained in Table 4.

TABLE 3. MEASURED ACRYLIC PRECURSOR YARN PROPERTIES[a]

Type	Denier	Load (lbs.) At Break	Load (lbs.) At 10%E	Initial Modulus (gpd)	Tenacity (gpd)
Acrylic I[b]	779	1.68	0.28	1.59	0.98
Acrylic II[c]	2951	9.89	0.43	0.66	1.52
Acrylic III[d]	4545	7.33	0.49	0.49	0.73

[a] With all the yarns except Acrylic III, 10 samples from 3 different cones were tested. The averages of the individual tests are given. For Acrylic III, 2 different cones were tested.

[b] Monsanto 100% Type 16 Acrilan Staple Acrylic Yarn.

[c] Monsanto Type 50% Acrilan 16/50% Acrilan B57 Staple Acrylic Yarn.

[d] Monsanto Type 40% B-94/40% S-90/20% B-90 Acrilan Staple Acrylic Yarn.

TABLE 4. PROPERTIES OF MONSANTO TYPE 16 STAPLE ACRYLIC YARN

Staple Length: 0-7 in.[a]

Number of Plies: 2[b]

Denier per filament: 5

Final Single-Ply Denier: 332

Brightness Classification: Semi-dull

Ply Twist (turns per in.): 9

State: Relaxed

Price: $1.40/lb [c]

Source: National Spinning Company, Washington, N.C.

Production: 60,000 lbs/week[c]

[a] Range obtained by the Turbo Break Process.

[b] The yarn is classified as 2-24's, worsted count.

[c] Quote by Mr. Tommy Younger, National Spinning Co. (1978).

PROCEDURES, RESULTS AND DISCUSSION

Enka Supreme Cordenka Rayon Precursor

During the initial studies on the Supreme Cordenka yarn, several facets of Figure 1 were different:

1. Tensioning godets were positioned before the first and after the last pyrolysis ovens.
2. Oven IV was not included in the pyrolysis line.
3. Air was not pumped through the drying oven.
4. No prescour bath was utilized.
5. A tensioning roller set-up was part of the Leesona winding unit, whereas the carbonized yarn was carried over a smooth plastic tensioning roll, through the traveller, around a metal roller, and then onto the package.
6. Temporary ovens available at Georgia Tech were utilized in these initial runs due to a delay in receiving the sophisticated Lindberg ovens from Fisher Scientific.

The rayon carbonization range procedure was initially conducted as follows:

Step 1. The yarn was pulled through the aqueous carbonization promotor impregnation bath of 16.8% w/w monosodium phosphate and 3.4% w/w boric acid at 25°C.[13] Flow rate was 12 in./min. throughout the range. The yarn passed over a rubber strip to remove most of the chemically-unbound water solution.

Step 2. The yarn then passed through a drying oven at 150°C containing static air (17" heating zone, 1 1/4" OD tube).

Step 3. The yarn passed over the first tensioning godet before entering the pyrolysis ovens. During the pyrolysis steps, only enough applied tension was utilized to avoid slackening of the yarn and subsequent contact with the tube walls.

Step 4. The yarn passed into the first oven of the pyrolysis range under static air conditions at 230°C (22" heating zone, 3/4" OD tube).

Step 5. The yarn passed into the second oven of the pyrolysis range under N_2 flow of 9 scfh, flowed parallel with the direction of yarn movement, at 275°C (17" heating zone, 1 1/4" OD tube).

Step 6. The yarn passed into the third oven of the pyrolysis range under combined CO_2-N_2 flows of 2 scfh and 6 scfh, respectively, at 1000°C (17" heat zone, 1 1/4" OD tube).

Step 7. The yarn passed over the second tensioning godet and was wound onto a tube package with the Leesona winder.

Appendix C details all of the pyrolysis runs conducted in the Enka Supreme Cordenka rayon precursor. These initial conditions were utilized in Run 1 of Appendix C. Start-up was accomplished by passing the initial yarn through the cool ovens, bringing the ovens up to the desired temperatures sequentially to insure proper conditioning, and marking the yarn section that signaled beginning of the desired product on the package. As shown in Appendix C, the yarn broke at a low temperature in Oven I of Run 1. Examination indicated that an uncontrolled exotherm had occurred under the conditions employed, with the yarn being badly fused. A flow of nitrogen was employed in Runs 2 and 3 with similar break temperatures. Two problems were observed in these initial runs:

1. Water was condensing in the tube of the drying oven under the static air conditions.
2. A viscous oil, suspected of being spin finish, condensed in the cool end of the tube of Oven I.

To circumvent the first problem, a small aquarium air pump was employed to "push" the hot, moist air through the drying oven before condensation occurred. The spin finish from previous experience was suspected of causing "flashing" in Oven I and this contributed to weakening of the yarn. The continuous line was thus modified to include a prescour bath inserted between the feed package and the carbonization promotor bath. Examination of the literature and consultation with Mr. Jerry Caldwell at American Enka revealed that ethanol and perchloroethylene were the best choices for removal of the spin finish from the yarns. Ethanol was chosen as the initial scource since it was water soluble, and a water sprayer was arranged immediately after the prescour bath to wash out the residual ethanol before promoter impregnation. Prescour was effected at 25°C.

It was also observed in the initial runs that severe mechanical damage due to excessive stress on the pyrolyzed yarn occurred as it passed

through the tensioning device apparatus of the Leesona winder. The winder was modified by attaching a pigtail guide to the original traveler so that the yarn passed directly from the plastic roller through the pigtail traveler and onto the package. The modification eliminated the majority of the yarn damage in subsequent runs.

Runs 4 through 6 in Appendix C were conducted under the modified conditions, and with higher N_2 flows in Oven I. No condensate was observed in the drying oven and Ovens I and II of the pyrolysis sector were manipulated successfully. However, breakage occurred at 300°C in Oven III under N_2/CO_2. Pure N_2 was used in Oven I, Run 4, whereas low air flow was used with the high N_2 flow in Runs 5 and 6. Temperatures were not altered. The air flow was supplied by a small air pump, and accurate determination of the air flow required insertion of an external flow meter in the air line. The main problem appeared to be either: (1) insufficient preconditioning of the yarn, or (2) too strenuous CO_2 oxidation in Oven III. It was observed that the yarn was not fully blackened after Ovens I and II, indicating incomplete low-temperature pyrolysis. The lack of reaction may have been due to the high N_2 flows "cooling" the yarn in relation to the remainder of the system, and hence inaccurate temperature profiles were being obtained.

In Runs 7 through 9, the gas flows were changed so that they counter-flowed with the direction of the yarn. The gas flows were lowered in Runs 7 and 8 to effect reduced cooling and thus to record a more accurate temperature of the yarn relation to that sensed by the pyrometer thermocouple. The result was breakage in Oven I, both with pure N_2 and with N_2-air mixtures. In Run 9, an intermediate N_2 flow of 12 scfh was employed with better results (Appendix C). In addition, CO_2 activation was eliminated from Oven III until the basic problem of obtaining completely carbonized yarn (reaching 1000°C in Oven III) without breakage was accomplished. The yarn obtained in Run 9 just before breakage at 400°C was unfused, jet-black in appearance, and lustrous. Contact with a match flame in air produced glowing but no flame, indicating considerable carbonization obtained during treatment on the pyrolysis range.

Variables that were altered in the next set of eight runs (Runs 10-17, Appendix C) on the temporary range included:

1. <u>Additional tension applied</u>

   Earlier runs had employed just enough applied tension to the yarn to keep it from sagging. A slight additional tension was applied between the godets, with some beneficial results (Run 17, Appendix C).

2. <u>Longer dwell times</u>

   The flow speed of the yarn through the process was slowed from 12 in/min to 8 in/min, again with apparent beneficial results. This indicated that insufficient dwell time for structure stabilization had been allotted in the earlier runs. Further research was thus warranted on optimizing dwell times while retaining the continuous nature of the process.

3. <u>Counterflow gas rates</u>

   A flow of 12 scfh of N_2 appeared necessary in the initial oven at <210°C to avoid breakage. In the second oven, a flow of 8 scfh appeared optimum.

Breaks continued to be a major problem in the research. "Hot spots" appeared to be developing in the yarn that were not controlled in the system. Several factors had become apparent by this stage:

1. Control in the simple ovens being used in the temporary range was not sufficient to prevent uncontrolled "spot" exotherms in the critical stabilization steps.
2. Critical temperatures for breakage were becoming evident, being defined as a maximum of 210°C in the first pyrolysis oven of the range and 325°C in the second oven.
3. The possibility that localized concentrations of non-extractable impurities in the precursor rayon (transition metal salts, or other rayon spin bath coagulants or spin finishes) were causing the "hot spots" was becoming more likely as the runs continued to fail.

After obtaining the Lindberg furnaces, they were taken through the prescribed "curing" cycles to dry out the wall components. One of the ovens was installed in the critical stabilization portion of the initial rayon line, and the yarn flow of the line was modified to accomodate the larger oven. Work then began on assessing the variables for optimum operation of the modified pyrolysis line.

After installation of the Lindberg, 19 runs were conducted on the line in the next set of experiments (Runs 18-36, Appendix C). The yarn was successfully manipulated through the pyrolysis ovens in many cases, with breaks occurring most often at the godet roll located beyond Oven III (max. 395°C before breakage). It was concluded that the radius of curvature provided too sharp a bend as the excessively brittle yarn passed over an idler arm located just below the godet. A plexiglass sleeve for the idler arm was constructed that increased the radius of curvature as much as possible while retaining a smooth surface. In addition, "hot spots" in Ovens II and III were still evident by the number of breaks, as well as the brittle nature of the yarn. Therefore, copper sleeves were produced to fit in the glass tubes of the ovens in order to provide more uniform heat distribution.

To decrease the time required to heat up the ovens to the proper temperature ranges on start-up, glass yarn was obtained from Owens-Corning to act as a "leader" for the rayon yarn. This approach allowed more rapid heating of the ovens, eliminating the slow staging temperature rise inherent when the rayon itself was utilized as the leader. The properties of the glass yarn were:

Denier: 1207
Breaking Strength: 11.2 gpd
Twist: 3.0 TPI
Upper Temperature Limit: 600°C

Using the modifications, Runs 37-51 in Appendix C were conducted. Runs number 44, 49, and 50 represented improvement in the process. The breaks occurred in these runs at the tension idler arm of the Leesona wind-up apparatus, which was past the godet idler problem point in the previous runs. The godet idler radius, increased by the sleeve made of solid plexiglass, thus appeared to be compatible with the system. The copper sleeves inserted in the glass tubes of the furnaces appeared to cut down on the number of oven breaks by giving more uniform heat distribution down the length of the tube, i.e., minimizing hot spots. The copper tubes degraded with time, however, at the high temperatures involved, and were later removed from the process line in the Avtex precursor runs.

Difficulty arose in determining if the breaks were due to chemicals, processing variables, or mechanical manipulations. As the fiber structure was greater than 90% carbon at the temperatures reached in the noted runs, mechanical manipulations were felt to be a major problem at this time. The windup mechanism was altered by incorporating a new motor and a speed reducer so that a constant speed could be maintained at the package rather than a constant tension. In addition, tension was maintained from this point by a simple free-standing tensioning guide rather than the godets previously used. The modified system allowed the yarn to follow a "straight line" path from the tensioning guide, located just after the carbonization promoter impregnation bath, all the way to the take-up roll. The mechanical manipulation of the yarn was thus decreased considerably from the godet variable tension windup system used in Runs 1-50 of the research.

Considerable concern continued, in view of the ease of breakage, that a major part of the problem lay in the rayon precursor itself. It was known that a number of chemicals are used by fiber producers in coagulation baths of rayon spin lines. These chemicals often include transition-metal salts, e.g., zinc salts, that could cause detrimental pyrolysis characteristics. According to the project's technical monitor, the 3M Corporation utilized several rayon precursors before finding one that did not give excessive breaks in earlier supply of carbonized yarn to Natick (see preface).

A final series of runs was conducted on the Supreme Cordenka precursor to attempt several radical approaches before drawing final conclusions on the feasibility of the yarn as a continuous carbon fiber precursor. The final runs made on the continuous rayon line with the Supreme Cordenka are located in Appendix C, Runs 51-101. The drive system modification (straight-line path through the ovens, minimal tension) detailed earlier and the use of a glass yarn leader to feed the initial rayon into the hot ovens worked smoothly. The Investigator thus conculded that the purely mechanical problems inherent in continuously processing the fiber had been surmounted. The ethanol desize bath was changed to perchloroethylene at Run 66, as perch is usually more effective (though not 100% efficient) than ethanol in removing any amine-containing spin finish from the yarn.

The starred runs 73-78 and 86-91 were conducted by completely bypassing the monosodium phosphate/boric acid carbonization promoter bath and utilizing pure N_2 in the ovens. A major problem in the process had been fused, stiff

yarn that was caused by deposition of the inorganic chemicals during drying. The fusion was carried through to the final carbon yarn. Discussions with industrial personnel also indicated that trace quantities of water maybe detrimental in the pyrolysis steps. The altered process gave much more flexible yarn than had been previously obtained and allowed higher carbonization temperatures at long continuous processing times without breakage. The carbon yields of the yarns without promoter were extremely low, however, and the yarn was excessively weak despite possessing improved flexibility. Excessive tar formation at higher pyrolysis temperatures also caused plugging problems in the tube of the final oven and eventually caused breaks. Experiments were begun with the non-promoter technique in which air was introduced in the initial ovens in various proportions under the theory that the added oxygen would facilitate crosslinking to some extent and therefore increase the char/volatiles ratio during high temperature pyrolysis. Run 87, Appendix C indicated that some improvement had occurred. A temperature of 850°C was reached on Run 87, and the temperature was held on the continuous process for several hours before breakage occurred. The carbon yield and yarn strength were still less than desired, however, and further experiments were unwarranted on the bypass system.

After considerable experimentation with by-passing the carbonization promoter bath and attempting to use oxygen as a char agent, the promoter bath (full strength) was reinserted in the line at Run 92 of Appendix C. Without the promoter, the char/volatiles ratio had been too low, resulting in unacceptable tar formation and weight loss. A short dwell-time fresh water bath was placed after the promoter bath to remove excess surface chemicals in an attempt to decrease fusion of the fibers.

The Enka yarn generally ran well up to 700°C, but higher temperatures again resulted in breaks. A fourth oven was placed in the line with a 9-inch pyrolysis length to attempt a more gradual profile to 1000°C on Run 101. Breakage occurred in Oven III, however, before Oven IV could be implemented in the stage-up.

After alleviating the mechanical problems of the system and investigating numerous combinations of variables during the 101 runs of Appendix C without successful development of a continuous, long-running process with a maximum temperature of 1000°C, the Investigator arrived at the conclusion

that the precursor rayon itself possessed inherent chemicals trapped in the yarn during production that prohibited good carbonization behavior. An attempt was thus made to coordinate with American Enka to determine if the company had conducted pyrolysis studies of its own on the Supreme Cordenka tire cord yarn (or close relatives of the precursor) and if potentially detrimental chemicals were present in the rayon.

After searching through the research hierarchy of American Enka Corporation, the author was routed to Mr. Dave Denning of the carbon group. Mr. Denning worked for approximately three years in Enka research toward development of a carbonizable rayon precursor that would not give frequent breaks in continuous processing. Although the research was terminated before the Supreme Cordenka Tire Cord required by the present contract appeared on the market, Denning related that he had investigated "off-the-shelf" Enka tire cord yarns that were forerunners of the Cordenka, and that were very similar in nature. Denning's overall conclusion after the research was that "off-the-shelf" rayon tire cord yarn did not lend itself to continuous carbonization. Enka, as had all manufacturers that produced carbon/graphite fiber from rayon, concluded that only a specially-spun rayon yarn could be carbonized effectively on a continuous basis without frequent breaks. The critical differences in terms of carbonization between the specialty rayon yarns designed specifically for good pyrolysis behavior and the commercial tire cord yarns were detailed as follows by Mr. Denning, based on the Enka work:

1. The optimum denier per filament found in the Enka research for pyrolysis was 2.3 dpf. The tire cord yarns are finer (~1.65 dpf) and suffer from different evolved gas diffusion rates than the specialty material.
2. The spin finish on the tire cord yarns contain a complex mixture of organic chemicals, including various amines. Rigorous scouring, solvent- or aqueous-based, does not completely remove the amines. Catalytic quantities of the amines were found by Enka to enhance localized rapid degradation, resulting in breaks. The specialty rayon yarns, therefore, do not contain these detrimental finishes.
3. The skin/core relationship of the yarn filaments was found to be extremely critical to pyrolysis behavior. A lower skin/core ratio than that found in commercial tire cords was found to be optimum, and therefore the specialty rayon filaments are spun under different

conditions than those of the tire cord.

4. Commercial tire yarn was found to contain large quantities of zinc salts from the spinning process. As the amines, zinc was found to promote rapid degradation of the fiber on pyrolysis. The specialty yarns, therefore, contain much less zinc than the commercial analogs.
5. Voids were found to be detrimental to continuous pyrolysis. The specialty yarns, therefore, are spun in such a manner as to minimize voids, unlike the tire yarns.

Mr. Denning's overall conclusion was that, based on his research experience, it was highly unlikely that the Supreme Cordenka Tire yarn specified in Contract No. DAAG17-76-C-0092 could be carbonized in a continuous fashion without excessive breaks. His conclusion and observations paralleled those made by the Investigator in Runs 1-101 of Appendix C.

The research on the Supreme Cordenka had been undertaken with the understanding that "off-the-shelf" tire cord yarns presented unique problems in carbonization that might prove insurmountable. However, the ready availability and high-volume production of the tire cord yarns compared to specially-spun precursors dictated that the initial research should be directed toward the Supreme Cordenka.

A major decision was thus warranted at this point in the project. The critical question that needed to be answered was whether the continual breaks were due to: (a) the nature of the specified rayon precursor, or (b) some flaw in the pyrolysis line or experimental approach. A decision was made by the Investigator, therefore, to obtain specially-spun rayon precursor that had been carbonized successfully by other researchers to HPGF to run on the rayon pyrolysis range. If the known carbon fiber precursor could be manipulated successfully on the range as constructed, the theory that the breakage problems reported in Runs 1-101 arose due to the problems inherent in the Supreme Cordenka yarn rather than flaws in the process itself would be confirmed, and the appropriate steps could be taken in the research.

After much searching and discussions with industrial personnel, the only commercially-available, specialty carbon fiber rayon precursor that could be identified was a yarn marketed by Avtex Fibers Corporation (previously FMC Corporation's Rayon Division). Mr. Phil Huff at the Charlotte

office of Avtex was contacted, and agreed to supply the Investigator with sufficient yarn (two 10-pound packages) to test the continuous process.

The properties of the Avtex precursor are contained in Table 2. Research was immediately begun on the new precursor, and the results are the subject of the following section.

Avtex Rayon Precursor

The conditions for Run 1 of Appendix D, the first run for the Avtex yarn, were the same as for Run 101 of Appendix C with the Enka yarn, i.e., no major changes were made in the operating line or conditions. The initial run was encouraging, with an 800°C temperature maintained in Oven IV for four hours without breakage. The main differences in the carbon yarn from the Avtex precursor over those of the Enka precursor were higher flexibility, higher strength, and much less fusion between filaments. The following Run 2 was the most successful run on the rayon pyrolysis line to this point in the research. A temperature of 850°C was maintained in Oven IV for several hours without breakage. The 850°C was found to be the maximum temperature for the short Oven IV, and a 22-inch Fisher tube oven was inserted to reach the desired 1000°C. The monosodium phosphate and boric acid (and/or their degradation products) sublimed out of the oven and built up deposits in the cooler portion of the quartz tube at the entrance end. The deposits grew with time and eventually caused "hanging" of the carbon yarn and, finally, breakage. The tube was shortened so that only approximately one inch extended from each end of the oven. Scanning electron micrographs of the carbon yarn from Run 2, Appendix D showed a smooth surface, good filament integrity, and minimal fusion between the filaments.

Based on the initial runs, which indicated that the yarn breakage in the Supreme Cordenka yarn was the fault of the precursor nature rather than the process, a total of seventeen additional runs under varying conditions were conducted on the rayon pyrolysis line with the Avtex rayon yarn (Appendix D, Runs 5-22). The goal was to initiate three separate runs from the start, and to carbonize the rayon continuously for a sufficient length of time without breaks to demonstrate the validity of the process. Repeatability was attained beginning with Run 16. Unlike earlier runs with the Enka rayon,

the only problem was breaks at the package during the early stages of the runs. The yarn was manipulated consistently through the various baths and ovens without breaks within the ovens themselves. A higher initial temperature (700-800°C) in Oven IV at the beginning of the runs appeared to minimize package breaks as the rayon followed the glass yarn leader through the pyrolysis sequence. In addition, it was discovered that early breaks were minimized by keeping a low N_2 flow in Oven I with no supplied air flow (beginning with Run 16 in Appendix D). Once these two factors were defined, consistent runs were possible. In Run 16, the yarn was carbonized continuously at 1000°C for five hours at a 12 inch/minute flow speed. The run was terminated arbitrarily at the five-hour point by the technician. The yarn was a shiny black in color, with good flexibility and little fusion, and had better strength than any yarn previously obtained in the research. Run 20 was a repeat of Run 16, with the system operated continuously for six hours at 1000°C before arbitrary shut-down. In Run 21, plans were made to run the system as long as possible until the N_2 supplies depleted and to continue operation as long as possible after the N_2 was exhausted, i.e., to assess operation with static air in the high temperature ovens. In Run 16, cutting off the N_2 in Oven IV for short periods had immediately resulted in a dulling of the yarn, indicating surface etching. Activation of the yarn by O_2 rather than CO_2 was thus considered to be a possibility. Run 21 ran overnight (15 hours), and the point on the package at which the N_2 was depleted was discernible by the sudden change from a black, shiny yarn to a dull, gray yarn. Greater tarring took place after the N_2 was exhausted, and the yarn finally broke at 15 hours due to hanging on the sticky tar on entering the glass tube at Oven IV. The research thus demonstrated that the Avtex precursor could be continuously carbonized at 12 inch/minute by the Georgia Tech process for indefinite periods of time, while the three fresh start-up runs (Nos. 16, 20, and 21) demonstrated the repeatability of the technique.

The carbonized yarn obtained from Runs 16, 20, and 21 (both dull and bright yarns) were tested for CCl_4 sorptivity in accordance with the contract specifications. Textile tests were conducted including tenacity, elongation at break, and denier. Scanning electron micrographs were also obtained to decipher surface characteristic differences in the yarns.

The results of the CCl_4 sorptive tests are located in Table 5. The sorptivity was low for the N_2-treated yarns, which was consistent with earlier literature reports. Elimination of the N_2 from Oven IV gave obvious etching of the fiber; the increase in sorptivity, however, was minimal (ca. 2.0%). The conclusion drawn was that some type of additional activation was necessary in order to attain the project objectives of 80% sorption by weight of CCl_4. Carbon dioxide was selected as the activation agent with the highest probability of success.

TABLE 5. CCl_4 SORPTIVE TESTS ON CARBON FIBERS FROM THE AVTEX PRECURSOR

	Conditions		Sample Weight		
Yarn Run No. (Appendix D)	R.H. (%)	T (°F)	Before CCl_4 (g)	After CCl_4 (g)	Increase (%)
16	85	72	0.42033	0.44731	6.42
20	85	72	0.43160	0.45983	6.54
21a*	73	72	0.59630	0.64072	7.45
21b*	73	72	0.58400	0.63924	9.46

*21a was the "bright" (N_2-treated) portion of the run, while 21b was the "dull" (decomposition gases/static air treated) portion.

Textile mechanical tests were conducted on the carbonized yarn to determine if project goals of denier and breaking strength were approached. Breaking strength and percent elongation to break were determined on an Instron Tester. The samples were mounted by taping one-inch sections of yarn at the ends and perpendicular to the yarn direction in order to provide a surface for the Instron jaws to contact without mechanical abrasion of the yarn. A total of ten one-inch breaks were conducted on each yarn sample, and the average breaking strength and elongation were determined. The yarn denier was obtained by carefully weighing five meter sections of the yarn and projecting the weight to 9000 meters. The results are shown in Table 6. The strength loss on carbonization was excessive (87%), and efforts were planned to retain more of the original tenacity through care-

fully-controlled processing variable alterations. The low elongation to break confirmed visual observations of the brittle nature of the yarns. The "dull" yarns obtained by eliminating the N_2 in Oven IV (yarn 21b) showed little strength loss from the N_2-treated yarn, indicating that air activation did not catastrophically affect mechanical properties.

TABLE 6. PROPERTIES OF AVTEX RAYON PRECURSOR AND RESULTING CARBON YARNS

Yarn Code	Denier	Fil/Yarn	Twist (TPI)	Breaking Strength (gpd)	Breaking Elongation (%)
Precursor	1650	720	2.0Z	3.08	11.5
16	1300	720	-	0.18	1.7
20	1100	720	-	0.17	1.4
21a*	1150	720	-	0.39	1.5
21b*	1200	720	-	0.38	1.8

*See footnote, Table 5.

Scanning electron micrographs (SEM's) were obtained for the Avtex precursor yarn and yarns obtained in Runs 21a and 21b: 1000°C/N_2-treated yarn (Run 21a), 1000°C/air-treated yarn (Run 21b). Reproductions of the SEM micrographs are contained in Figures 5-7. The Avtex precursor consisted of smooth-surface filaments, with each filament having an essentially circular cross-section with some wavy striations apparently caused by shear forces and filament "wobble" or twist on exiting the spinneret hole. SEM's of the N_2-treated 21a yarn revealed good retention of filament structure with little etching or fusion. However, chemical crystals were clustered at various points on the surface of the filaments. Magnification at 1000x revealed needle crystal clusters. The crystals apparently had "grown" on the surface through sublimation/decomposition/deposition of carbonization promoters from the inside of the fiber.

Earlier runs had exhibited a build-up of white solid at the entrance

FIGURE 5. SEM Micrographs of the Avtex Rayon Precursor Before Carbonization

FIGURE 5 (cont.)

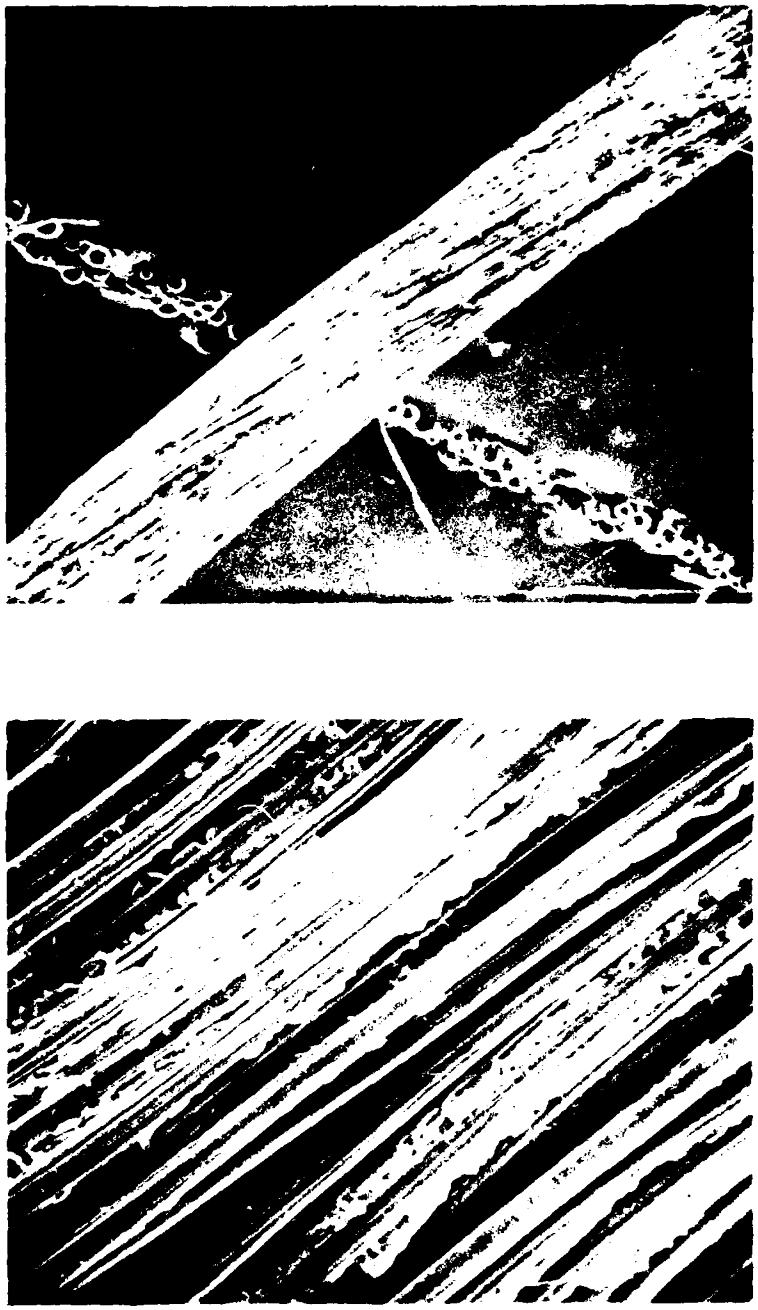


FIGURE 6. SEM Micrographs of Avtex Rayon-Based Carbon Fibers Pyrolyzed to 1000°C Under Nitrogen

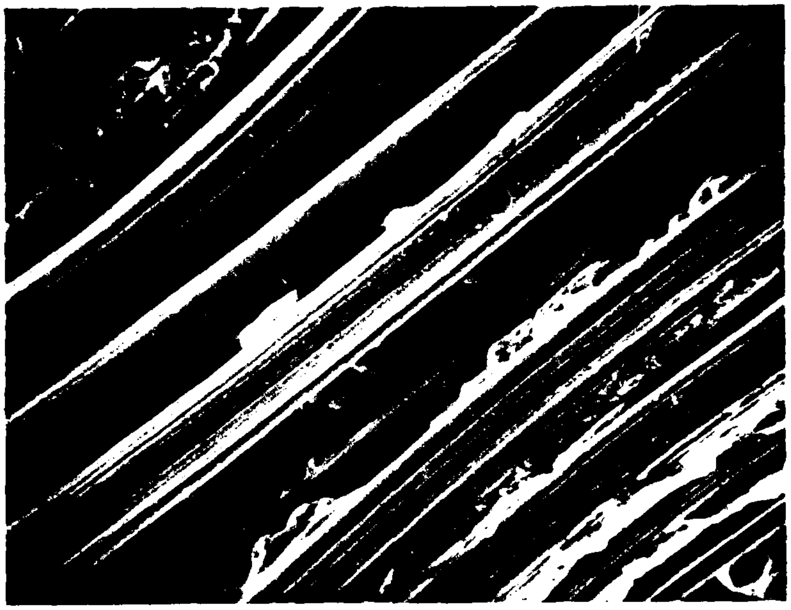


FIGURE 6 (cont.)

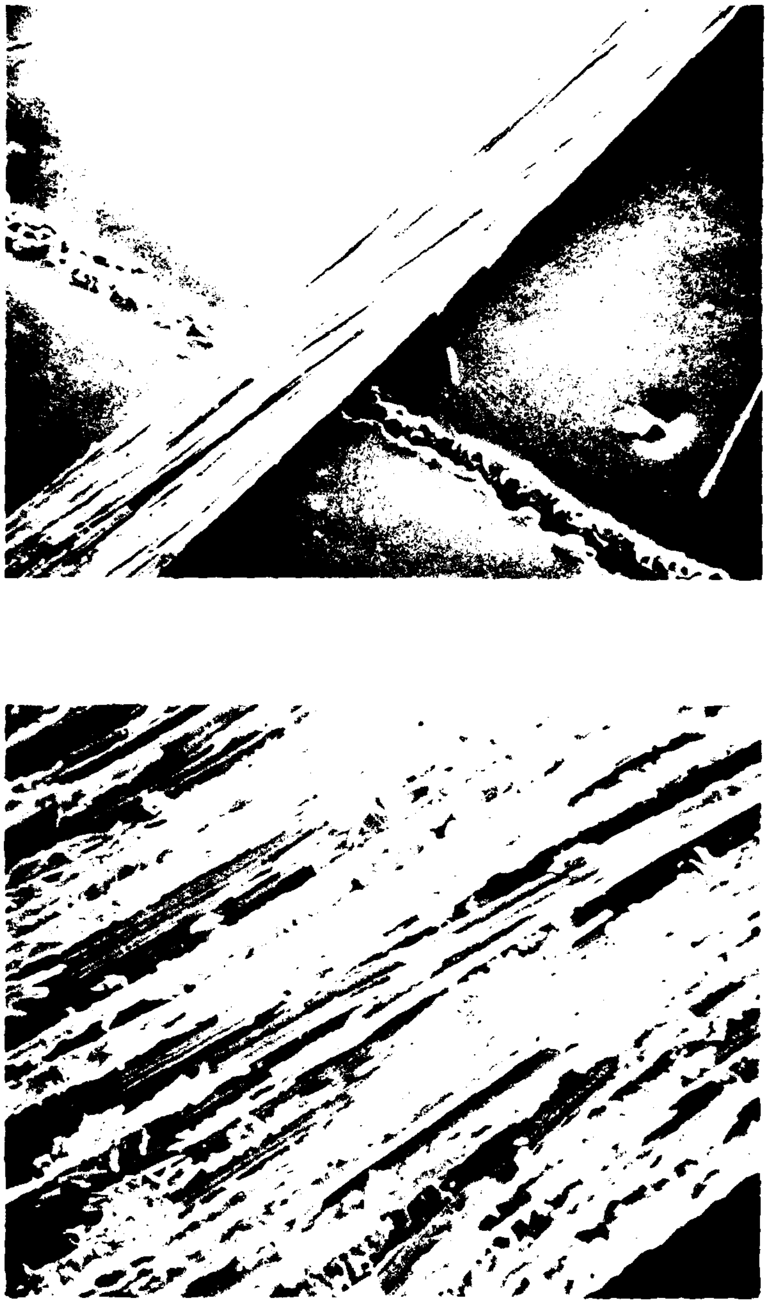


FIGURE 7. SEM Micrographs of Avtex Rayon-Based Carbon Fibers Pyrolyzed to 1000°C Under Static Air

FIGURE 7 (cont.)

tube of the 1000°C oven with N_2-flow, indicating sublimation/degradation of the H_3BO_3 and/or NaH_2PO_4 chemicals. The NaH_2PO_4 exists as the monohydrate, which thermally decomposes at 210°C. The boric acid converts at 169°C to HBO_2, and further decomposes with water loss at 300°C.

SEM's of yarn 21b, which had been treated at 1000°C with static air instead of N_2 in the final oven, revealed an even higher volume of crystal deposition with smooth filaments and a slightly higher degree of fusion than had been observed in the 21a N_2 run. The N_2 flow apparently had swept a portion of the sublimate/decomposition chemicals from the chamber before they could be incorporated in the crystal growth.

The SEM's revealed several other interesting characteristics of the yarns. When end sections of broken or cut filaments from any of the carbonization runs were examined, most of the filaments had an open slit running down the entire length of the filament. The slits were not present in the Avtex precursor. A plausible theory for the slits was that the impregnation solution containing the carbonization promoter did not fully diffuse to the interior of the filament, resulting in the center of the filament being untreated with flame retardant, and thus the cellulose at that point was literally burned away during the pyrolysis treatment. The slits were likely a primary factor in the low tenacities exhibited by the carbon fibers (see Table 6), as only the outer sheath was still available to sustain the load.

Peters' 1969 3M patent on carbonization of rayon revealed several references to heating the impregnation bath, with "5-minute immersion in a "near boiling" salt solution followed by removal of excess solution to give 100% wet pickup of salt solution" reported to be preferred.[13] Heating of the impregnation bath would cause swelling of the hydrophilic rayon filament, and therefore increase the diffusion of the chemicals completely to the fiber center (c.f., dyeing operations on rayon). Earlier experimentation on heating the impregnation bath had been unsuccessful mainly due to insufficient stirring, resulting in localized superheating, decomposition/precipitation of the salts, and ruination of the bath. The bath heating system and procedure were designed in later runs to give temperatures of 150°-212°F in order to promote diffusion and attempt elimination of the slit problem.

Perusal of the 3M patent also revealed the following statement:[13]

> "The (carbonized) product, after cooling, may be washed to remove soluble materials that are present and which might adversely affect desired properties of the product."

Rinsing of the carbonized product between the 1000°C oven and the wind-up of the package was therefore projected to improve the mechanical properties as well as providing greater macropore sorptive area due to elimination of the crystalline salts. It was thus decided, as part of the research, to explore the rinsing approach.

In the next series of runs on the Avtex rayon precursor, Runs 22-37 of Appendix D, attempts were resumed to bleed in carbon dioxide (CO_2) as a sorption activation atmosphere in Oven IV, but still without a rinsing step. In Run 24, after continuous processing at 1000°C had been achieved with N_2 in Oven IV, the yarn was marked and CO_2 was bled into the oven at a 10 scfh N_2/2 scfh CO_2 ratio without stopping the yarn drive. The yarn immediately converted from shiny black to a silver grey in color, indicating severe etching. Excessive yarn breakage followed soon afterwards, and the run could not be maintained. On cleaning the quartz tube of Oven IV after Run 24, it was observed that the tube had cracked catastrophically. A white layer of material was on the surface of the tube, indicating possible oxidative attack by the CO_2. Consultation with glass experts determined that water-free quartz was desirable in order to prevent CO_2 attack in the necessary temperature range (1000°C). None of the special quartz could be found locally, and had to be ordered. Alterations were made at this point in the optimum physical system (ovens, tubes, etc.) to compensate for the shattered tube and avoid shutdown of the process line; however, no successful runs were accomplished with the altered systems with N_2 in the final oven (see Runs 25-37, Appendix D). The modifications thus resulted in a loss of control of the process that could not be overcome.

After replacement of the oven tubes with water-free quartz, research on the Avtex rayon pyrolysis line concentrated on conducting a long, continuous carbonization run at 1000°C in which the N_2/CO_2 ratio could be varied at different times in order to collect a spectrum of yarns at different ratios which could be tested for textile/sorptive properties. The runs

conducted are detailed in Appendix D, Runs 38-51. Samples a-d of Runs 45 were treated at the following N_2/CO_2 ratios at 1000°C:

Run Code	N_2(scfh)	CO_2(scfh)
45a	5.5 (11)	0.5 (1)
45b	5.3 (6.3)	0.8 (1)
45c	5.0 (5)	1.0 (1)
45d	4.8 (3.6)	1.3 (1)

The values in parentheses are the normalized ratios relative to CO_2. The line ran continuously for 13 hours with no problems until the N_2/CO_2 ratio was lowered to 3.6:1, at which point the yarn began breaking almost immediately and the run could not be maintained (Run 45d). The yarn was mainly degraded at the break point of Run 45d, exhibiting "bubbles", fusion, and extremely weak strength. The preliminary experiments thus defined an approximate N_2/CO_2 ratio of 4:1 as being a limiting value for continuous processing under the utilized conditions.

In view of the successes on the rayon line with the Avtex precursor, a large stainless steel pigtail was attached to the traverse of the Leesona winder to attempt traverse winding of the carbonized yarn onto the package (beginning at Run 46 in Appendix D). Run 49 was successful at higher temperatures under N_2 and with bleed-in of a 7:1 ratio of N_2/CO_2. The technician reported that the power voltage was at a point that normally reached 1000°C on the pyrometer, indicating a thermocouple malfunction. Thus the 900°C readout was probably low, with the true temperature being around 1000°C from the past experience at the recorded voltage reading.

The experiments confirmed that the carbonized yarn had sufficient mechanical properties to allow traversal onto the package. The pigtail was constructed so that the ring could be removed from the traverse at will and therefore not interfere with the straight line flow onto the package. This arrangement was necessary in order to start up the line without traverse interference, and to have the capability to enter the traverse action through the pigtail loop by hand. A traversed package is desired to facilitate removal of the filling yarn from the package in weaving or braiding.

SEM's of the 1000°C N_2/CO_2-treated yarns, Runs 45a-45d of Appendix D, revealed similar chemical decomposition as had been observed on the SEM's

of Runs 21a and 21b ($1000^{\circ}C/N_2$-treated). The micrographs of Run 45b (6.3 N_2/1 CO_2) and Run 45c (5 N_2/1.0 CO_2) are shown in Figures 8-9. The needle crystal growth on the surface closely resembled the structure of that observed on the Run 21a yarn in particular (Figure 6). Higher magnification on another SEM revealed that the crystals consisted of extremely uniform needles growing mainly perpendicular to the fiber surface (Figure 10). X-ray elemental analysis coupled with the high magnification SEM revealed that the elements consisted chemically of phosphorous and sodium, that phosphorous was present in the solid in huge excess, and that little sodium was present (Figure 11). The instrument did not have the capability of analyzing for lighter elements, such as boron or oxygen. The deposit contained practically no sodium, and thus likely consisted of a degradation product of NaH_2PO_4. The possibility of boron being incorporated in the phosphorous degradation product was not eliminated by the SEM/X-ray analysis.

In the 5:1 N_2/CO_2 ratio yarn, Run 45c, some of the filaments exhibited infrequent "bubbles" on the surface that appeared to be caused by escaping gases or sublimate pushing the surface of the softened filament outwards, resulting in the perturbation. The bubbles were not as prevalent in the 6.3:1 N_2/CO_2 ratio yarn and were absent altogether in the Avtex filament, the N_2-only filaments, and the air-only filaments, indicating that increased CO_2 concentration was responsible for the surface bubbles. No severe surface etching was evident, however, on the 5:1 N_2/CO_2 ratio yarn.

When the yarn filaments were cut and the end sections examined by SEM, most of the filaments had an open slit running down the entire length of the filament. The SEM's are contained in Figure 12. The slits were similar in appearance to those detailed in Figures 6-7 for Runs 21a and 21b of Appendix D, and reiterated the need for improving the diffusion of the carbonization promoter solution to the center of the fiber diameter (refer to the discussion on the postulated cause of the slit phenomena earlier in this section).

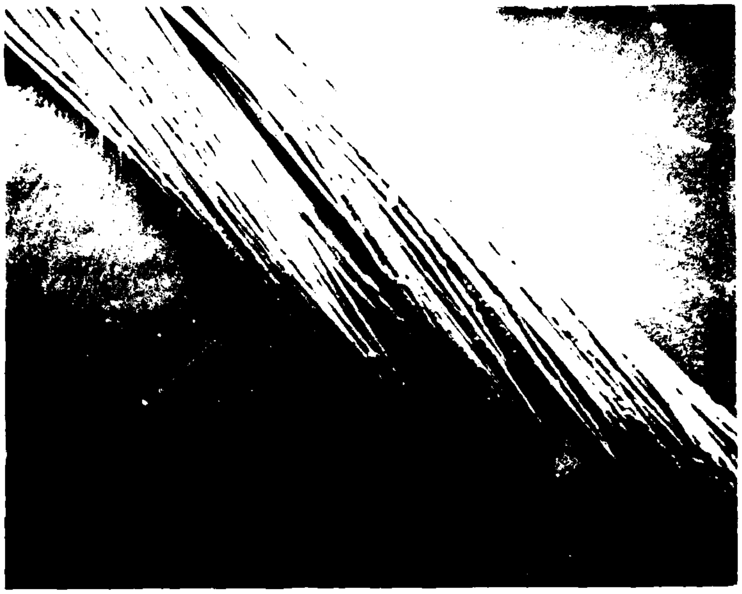


FIGURE 8. SEM Micrographs of Avtex Rayon-Based Carbon Fibers Pyrolyzed at 1000°C Under 6.5:1 Nitrogen:Carbon Dioxide Atmosphere

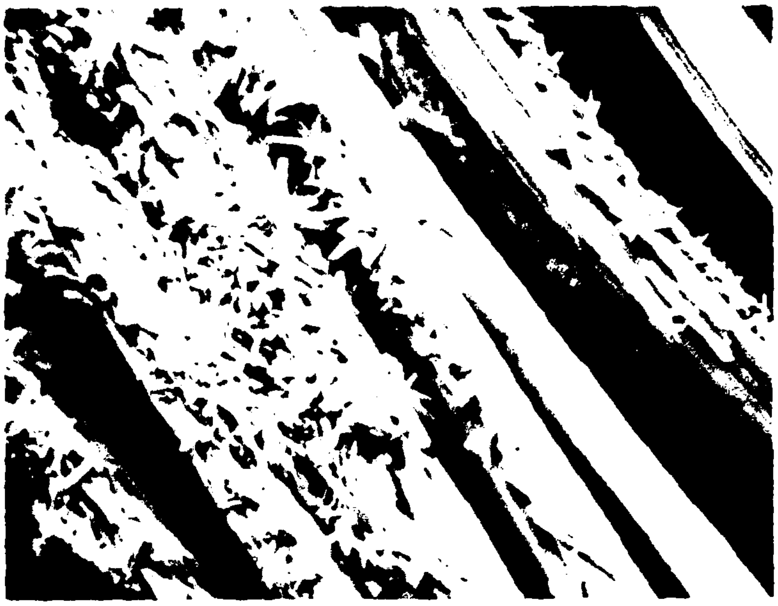


FIGURE 8 (cont.)

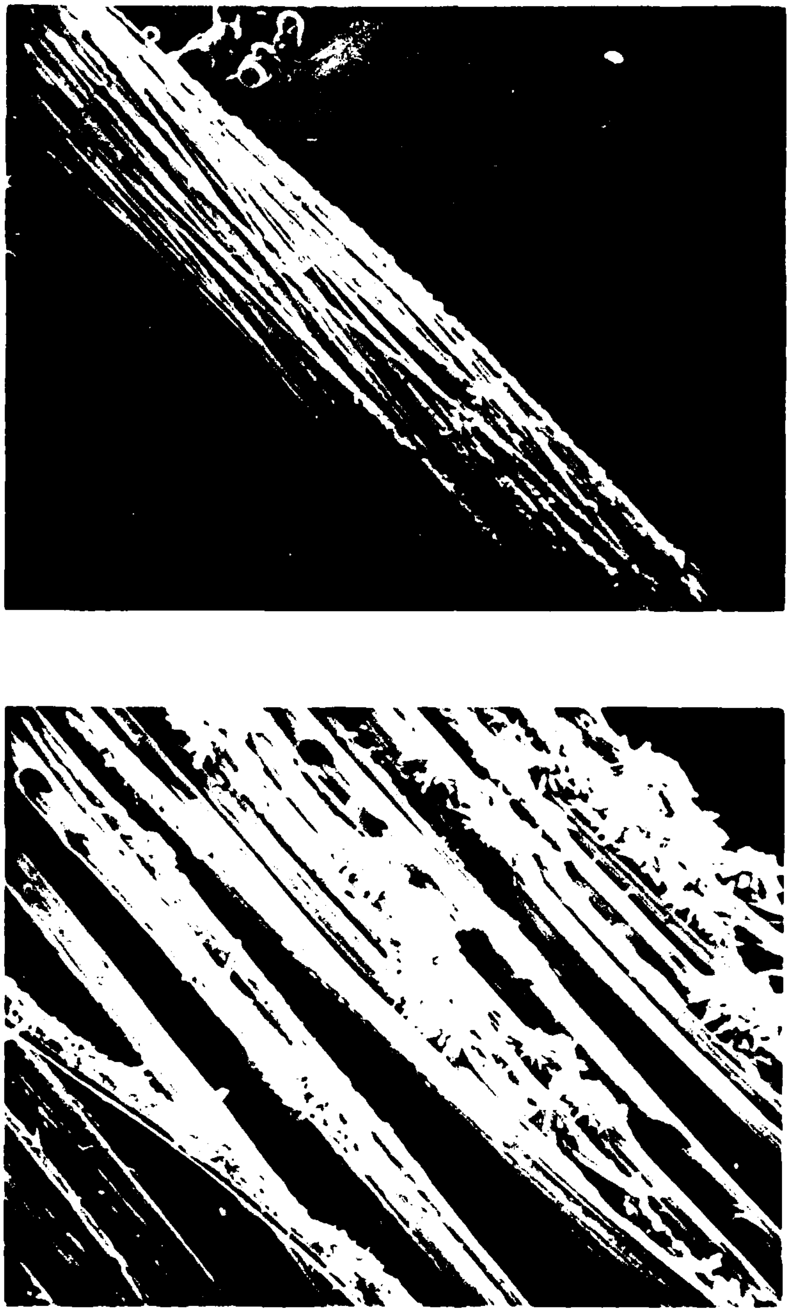
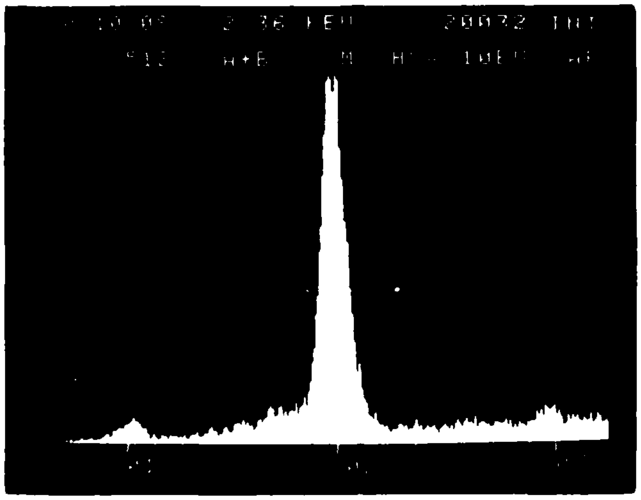


FIGURE 9. SEM Micrographs of Avtex Rayon-Based Carbon Fibers Pyrolyzed at 1000°C Under 5:1 Nitrogen:Carbon Dioxide Atmosphere

FIGURE 10. High Magnification SEM Micrographs of Chemical Crystal Growth Observed on Avtex-Based Carbon Fibers Pyrolyzed at 1000°C Under 5:1 Nitrogen:Carbon Dioxide Atmosphere



Na P Ag
Elements

FIGURE 11. X-Ray Elemental Analysis of Crystal Growth Detailed in Figure 10.

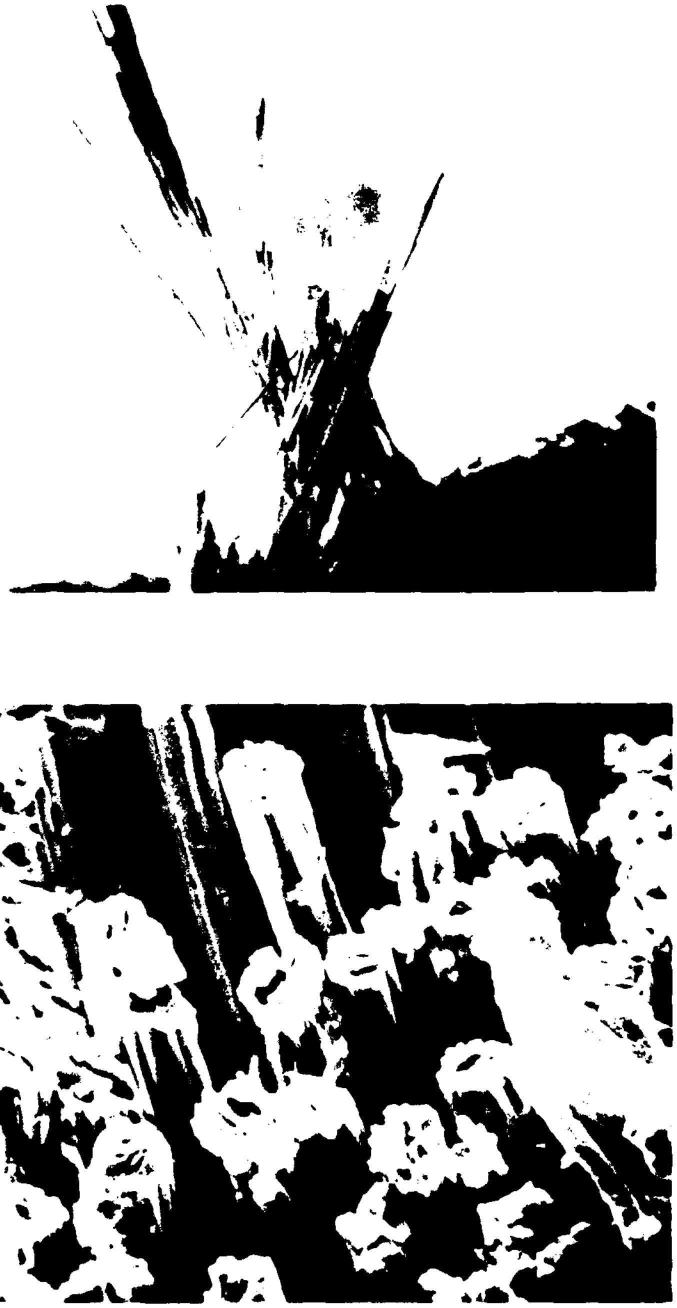


FIGURE 12. SEM Micrographs of End Section View of Avtex-Based Carbon Fibers Pyrolyzed at 1000°C Under 5:1 Nitrogen:Carbon Dioxide Atmosphere

FIGURE 12 (cont.)

CCl_4-sorptive tests were conducted under standard conditions on the yarn from Runs 45a-45c in Appendix D. The individual yarns were placed in a glass jar and the assembly dried for 5.5 hours at 130°C in an oven. The system was then weighed to five decimal places and mounted in a dessicator containing saturated CCl_4 vapor. The system was suctioned off briefly to remove water vapor and air, and the fiber allowed to sit overnight (18 hours) in the CCl_4 environment. The assembly was then removed and weighed immediately to determine CCl_4 adsorption. The results are recorded in Table 7. Some increase was observed as the CO_2 ratio increased, but the adsorptivities did not reach those recorded for the 1000°C/air-treated yarns in Table 5. Future research was thus warranted to increase the sorptivity, possibly with mixed-gas systems in the 1000°C oven to properly activate the carbon.

TABLE 7. CCl_4 SORPTIVE TESTS ON CO_2-ACTIVATED CARBON FIBERS FROM THE AVTEX PRECURSOR

Yarn Code	N_2/CO_2 Ratio	Sample Weight Before CCl_4 (g)	Sample Weight After CCl_4 (g)	Increase (%)
45a	11:1	1.09579	1.14047	4.1
45a	11:1	1.09938	1.16169	5.6
45b	6.3:1	0.54479	0.58759	7.9
45b	6.3:1	1.08766	1.16809	7.4
45c	5:1	1.52824	1.65923	8.6

Textile tests were also conducted on the yarns from Runs 45a-45c in Appendix D. The results are located in Table 8, with Avtex precursor properties repeated for comparison. The Avtex precursor, not being designed for tire cord use but instead for good carbonization characteristics, had a considerably lower breaking strength than the Enka Supreme Condenka yarn used initially in the project (3.1 gpd versus 5.1 gpd). The lower starting strength dictated a lower target strength for the carbon yarn (1.0-1.5 gpd), considering a 60% drop in strength common in all pyrolysis procedures for rayon in the 1000°C range.[4] Higher strength could be achieved by increasing

the temperature in the final oven to 1400-1500°C. When carbon fibers are heated to the higher temperatures, molecular rearrangement takes place, reordering the carbon structure. In effect, the carbon is further crystallized at the higher temperatures, resulting in higher strength but a collapsed micropore structure. Increasing the strength of the carbon yarns by purely thermal means above 1000°C must therefore be balanced against detrimental effects on sorptivity.

TABLE 8. YARN PROPERTIES OF CO_2-ACTIVATED CARBON FIBERS FROM THE AVTEX PRECURSOR

Yarn Code	Denier	Breaking Strength (gpd)	Breaking Elongation (%)
Avtex Precursor	1650	3.1	11.45
45a	1200	0.21	1.41
45b, 1	1200	0.22	1.45
45b, 2	1100	0.24	1.61
45c	1100	0.20	1.09

The carbonized yarns from Runs 45a-45c showed a 93% drop in strength by the Instron test. The results were suspected to be misleading, however, due to the massive chemical deposition observed on the surface by SEM. The textile unit of "grams per denier" is dependent on the load in grams required to break a yarn of a certain weight per 9000 meters (denier). If the weight were increased substantially by a non-load bearing constituent, i.e., chemical crystals, the yarn weight would be erroneously high and the tenacity, therefore, low. The Peters' 3M patent[13] had listed a denier of 800 for carbon yarn obtained in a similar process from precursor yarn of the same starting denier (1650), whereas the denier of the obtained carbon yarns in Table 8 varied from 1100-1200 denier. The patent gave no indication of whether the carbon yarn was washed and dried before the denier was determined. As an example, using a breaking strength of 454 g, and using 1150 denier and 800 denier as the yarn weights per 9000 meters, breaking strengths of 0.39 gpd and 0.57 gpd, respectively, are obtained, comprising a 46% "increase" in the strength.

Future tests were thus warranted with the carbonized yarns after thorough washing and drying to determine if the denier (and therefore the calculated strength) had changed appreciably.

The water-free quartz obtained for the 1000°C oven apparently alleviated the tube breakage problem and exhibited no breakage with CO_2 introduction through Runs 49. Further monitoring of the tube surface was conducted as runs continued to insure that the breakage problem was solved.

The next series of experiments were designed to evaluate heating of the carbonization promoter bath to improve diffusion into the center of the rayon filaments, and therefore eliminate the center-filament, lengthwise slits that had been observed in the earlier runs by SEM (Figures 6-7 and 12). A variable-speed electric stirrer was mounted above the impregnation bath, and stirring was effected by a glass rod/teflon paddle system hooked to the stirrer shaft. The stirring action had to be controlled carefully to avoid excessive turbulence which caused yarn tangling as the rayon passed through the solution. Stirring was deemed necessary to avoid localized superheating of the concentrated salt solution and possible degradation of the chemicals. The stainless steel trough containing the bath was then placed on three flat-top hot plates. Runs 51-62 of Appendix D were conducted with the bath temperature held at 60-65°C with stirring. In addition, a continuous rinsing system to investigate washoff of deposited chemicals and its effect on properties was placed after Oven IV, beginning with Run 54. The system, termed a cascade rinse, consisted of a tubular stainless steel pipe that was capped at one end and connected to a length of tubing at the other end through which faucet water was fed. A line of small holes was drilled down the length of the pipe to create the desired spraying action. The pipe, with the line of holes toward the yarn, was clamped above and perpendicular to the direction of the traversing yarn between Oven IV and the winder package. The carbonized yarn was then sprayed thoroughly as it passed continuously below the spray.

As shown in Runs 51-62 of Appendix D, the two modifications acted in concert to introduce a breakage problem that had been largely avoided in the preceeding Avtex precursor trials. The breakage was at the low-temperature positions (Ovens II and III), and was first postulated to be due to a 15-minute log time during which the rayon remained stationary in the short rinse bath positioned after the impregnation bath to remove excess surface chemicals and lag

thereby avoid interfilament fusion. The lag time resulted while the overfeed of the glass yarn leader was traversing the pyrolysis line. Several modifications were attempted, however, without success. For example, the ovens were bypassed completely with the initial rayon to insure proper chemical pretreatment of the freshly-fed yarn. Once proper treatment was insured, the rayon yarn was directly spliced into the glass leader and the range traversed.

In runs 63-70 of Appendix D, the temperature of the carbonization promoter bath was lowered in an attempt to regain processibility. However, breaks continued throughout the series. The force of the water striking the yarn at the rinse stage apparently caused the breaks in Runs 63-70.

For the final series of runs conducted on the Avtex rayon precursor in the reported research, fresh baths were prepared for the entire carbonization range (perchloroethylene scour, carbonization promoter bath, and after-rinse static bath). The cascade rinse was turned off, the promoter bath was not heated, and only nitrogen was bled to Oven IV. Runs 71-74 of Appendix D were unsuccessful, with breaks in Ovens II and III. In Run 75, the 1000°C level was reached, and CO_2 was bled in successfully to reach a 5:1 N_2/CO_2 ratio. The system ran well for one hour, at which time the water flow to the cascade rinse was reintroduced. Immediately, breakage occurred at the weak point in the line (Oven II). The additional tension developed in the yarn line by the water striking the yarn was thus sufficient to break the low-strength material.

The cascade rinse system was then modified by clamping a solid glass rod along the hole line in the stainless pipe. When the water was turned on at low volume, the flow created a thin film of water along the glass rod. The yarn was then passed adjacent to the glass rod's surface, and hence the carbonized material was gently rinsed as it passed through the thin layer of water.

Beneficial results were immediately evident using the modified rinse system. Runs 76-81 of Appendix D were conducted using the gentle rinse. Runs 76 and 81 ran well, with CO_2 introduced successfully. These runs thus confirmed that continuous rinsing was feasible as long as extremely gentle conditions were utilized.

Batchwise soaking experiments were conducted on the yarn obtained in Run 81 of Appendix D, and SEM micrographs were obtained before and after washing. As shown in Figure 13, the yarn from Run 81 that had been exposed to the modified

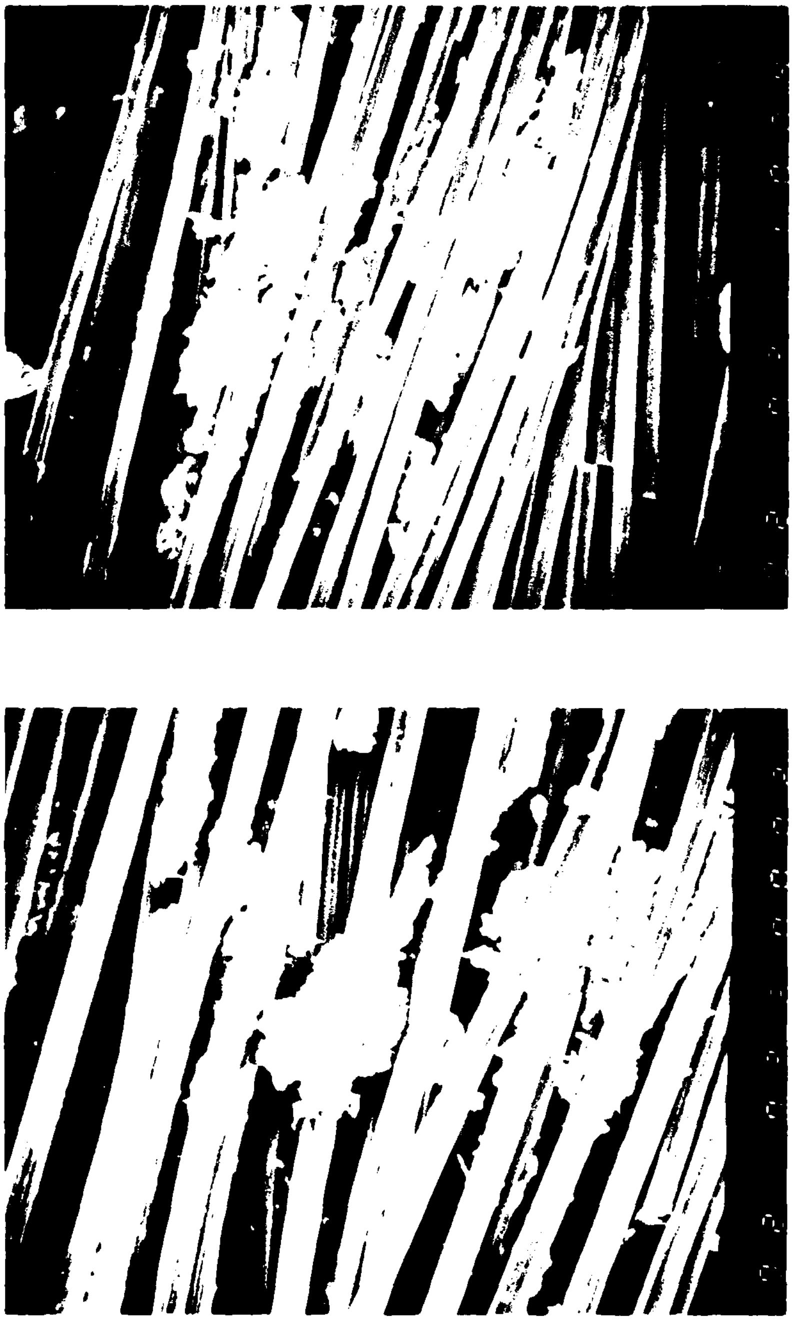


FIGURE 13. SEM Micrographs of Avtex-Based Carbon Fibers Pyrolyzed at 1000°C Under 5:1 Nitrogen:Carbon Dioxide Atmosphere Followed by Mild Continuous Rinsing

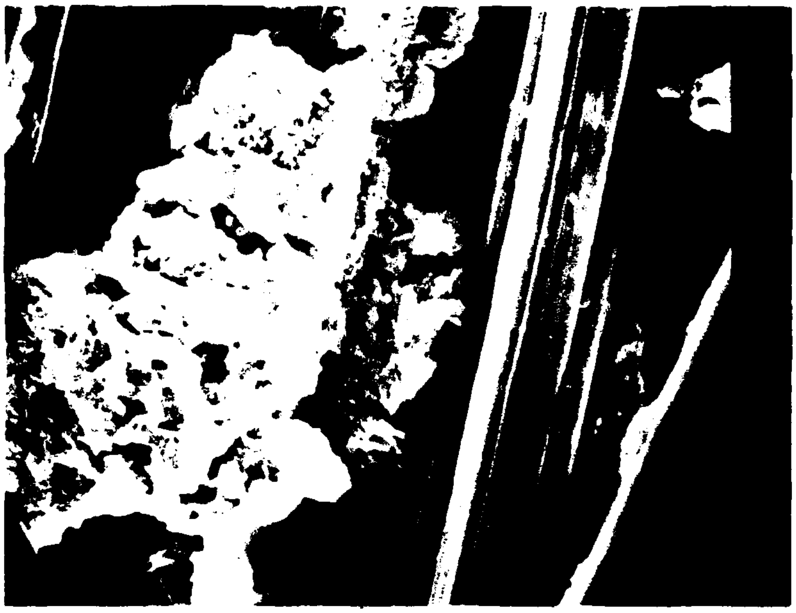


FIGURE 13 (cont.)

cascade rinse still possessed some chemical deposits, but much less than had been observed earlier without the continuous rinse (Figures 6-9). A skein of the same carbonized yarn was placed in a beaker of water at room temperature and allowed to stand twelve hours without agitation. The yarn was then carefully removed, blotted between pieces of filter paper, and finally dried in an oven at 125°C for two hours. SEM micrographs were then obtained on the yarns. As seen in Figure 14, the carbonized yarns were totally devoid of chemical deposits after the soaking experiment. The results confirmed that complete removal of the chemical deposits was possible, but indicated a more thorough rinse than had been utilized in Runs 76-81 was necessary to continuously clean the yarn.

Static Tests on Rayon Precursor

A series of scouting tests was conducted with the Supreme Cordenka rayon on the static system. The yarn was dipped in separate beakers containing respectively perchloroethylene, carbonization promoter bath, and pure water. The yarn was then suspended in the quartz tube of the static oven, and placed under a slight tension by tying small weights at the ends of the yarn protruding from the furnace. The temperature was staged up and held at critical points to simulate as closely as possible the treatment of the yarn manipulated through the continuous pyrolysis line (Figure 1) and under temperature/time/atmosphere profiles similar to those reported in Appendices C and D.

The initial experiments were conducted with phosphoramide-based flame retardant formulations from Monsanto, MCC-100 and MCC-300 (Appendix E, Runs 1-4). These were the only non-inorganic salt flame retardant formulations identified that gave desired high char/volatiles ratios with cellulosics.

The results of the initial static experiments are contained in Appendix E. Similar results to the continuous line (Appendix C) were obtained, with breakages occurring at less than 850°C. The formulations thus initially did not appear to be viable alternatives to the monobasic sodium phosphate/boric acid system already employed in the continuous range.

Additional static tests were conducted utilizing Monsanto's phosphoramide-based MCC-100 and MCC-300 flame retardants and also reduced concentrations of NaH_2PO_4/H_3BO_3 promoter baths (Appendix E, Runs 5-12). The reduced concentration runs were made to determine if those reported in the Peter's patent[13] were too high for good yarn flexibility, and whether an intermediate

concentration would give a high char:volatiles ratio while maintaining flexibility. The MCC-100 and MCC-300 continued to give discouraging results. The reduced-concentration NaH_2PO_4/H_3BO_3 solutions, however, showed promise, with a temperature of 733°C reached before breakage using half-strength solution.

Efforts were initiated to obtain a different phosphoramide-based flame retardant from Exxon Corporation that appeared to be headed for commercial production for study as a candidate in the static test. Mr. Harry Dittmar of Exxon Corporation subsequently informed the Investigator that limited quantities of the flame retardant prohibited a donation to the project for static tests. He suggested a contact at Cotton Incorporated that earlier received a substantial quantity of the material for a possible donation. This avenue was also closed, however, as Cotton Incorporated was unable to relinquish any of its supply of the formulation due to its own research needs.

At this point in the project, two factors surfaced which precluded any further static tests. First, Monsanto informed the Investigator that production had been halted on the MCC-100 and MCC-300 formulations, and that the company had no future plans to enter an alternate phosphoramide flame retardant onto the market. Second, the decision was reached to eliminate the Enka Supreme Cordenka rayon yarn as a candidate for continuous carbonization. Due to manpower and funding limitations, the subsequent successes with the Avtex rayon precursor on the continuous pyrolysis line (Appendix D) further precluded any additional research on the static unit with rayon.

Acrylic Yarn Precursor

The initial effort on the staple acrylic precursor research was directed toward construction of the second continuous process line detailed in Figure 4 and described in the apparatus and chemicals section of this report. The line was designed to consist of a scour bath, an impregnation bath, a drying oven, and an 18-foot length of heated glass tubing for preoxidation followed by a Lindberg furnace for carbonization. Following the flow of Figure 4, the yarn initially travelled through a chemical sequence consisting of a perchloroethylene bath to remove finishes and oils, water rinse, impregnation in a sodium glyceroxide-glycerol bath, water rinse, and passage through a drying oven. The sodium glyceroxide-glycerol acted as a swelling agent for the acrylic fiber, and provided initiation sites for thermally-activated nitrile

FIGURE 14. SEM Micrographs of the Carbon Yarn Pictured in Figure 13 After Soaking in Water

cyclization necessary for ladder polymer formation. From the drying oven, the yarn passed to the glass tubing furnace consisting of three 6-foot lengths of 2-inch DIA pyrex tubing connected with jointed ends and capped with an adapter containing yarn and gas flow connections. The furnace was constructed by Georgia Tech personnel. Nichrome wire was used as the heat source. The wire was wrapped on the tubes in such a way as to give a temperature gradient from 200°-225°C at the entrance tube to 300°-325°C at the exit tube under static air. The furnace power source was three variacs, one for each length of tubing. Thermocouples were placed at predetermined points along the 18-foot length to carefully monitor the temperature gradient. The wire-wrapped tube was enclosed in asbestos tape, and the entire inner-tube assembly enclosed in a 3-inch diameter glass sleeve covered by foil-backed fiberglass insulation. The line was completed with a Lindberg furnace held at 900°-1000°C under N_2. The Investigator, from previous experience and reported literature,[31] projected that the cyclization promoter applied in the impregnation bath followed by slow, careful preoxidation would provide proper stabilization to carry the yarn directly from 300°-325°C to 1000°C continuously without long intermediate stage-up cycles.

The most difficult task in constructing the acrylic pyrolysis line lay in wrapping the components of the 18-foot tube furnace with the proper pitch of Nichrome heating wire in order to attain the desired temperature gradient down the entire length of the unit. If the pitch angle of the wire helix was too low, electrical resistance was excessively high due to the long length of wire, and the end of the tube section furthest from the power connection did not receive enough current to heat to the proper temperature. If the pitch angle was too high, insufficient heat was transferred through the glass walls to reach the desired temperatures. An intermediate approach thus was adopted in which the cool end of each length of tube was wrapped at a high pitch angle, and the angle was gradually reduced as the wire wrap progressed down the length of the 6-foot tube section until, at the hot end of the tube, the pitch angle was considerably lower than the original cool end wrap. Using this technique, the temperature profile detailed in Table 9 was eventually, after many trials and revamping, attained.

TABLE 9. TEMPERATURE PROFILE OF 18-FOOT TUBE FURNACE

Tube Section (6-foot length)	Cool End (°C)	Hot End (°C)
1	200	250
2	250	290
3	300	310

After completion of the acrylic pyrolysis line, several runs were attempted with the National Spinning Company sweater acrylic yarn consisting of Monsanto Type 16 staple fiber (see Table 4 for a full property description of the yarn). Early problems revolved around the hot sodium glyceroxide carbonization promoter bath.[31] The glycerine "smoked" badly at the high temperatures, resulting in a worker safety hazard as well as coating of area instruments. Attempts at running the yarn through the promoter bath at lower temperatures did not give sufficient stabilization, and the preoxidation furnace (18-foot) could not be manipulated without breakage. The yarn could not be held stationary in the promoter bath during warm-up, as excessive swelling and some solubilization was observed. The Owens-Corning glass yarn leader used on the rayon line, which was inert to the chemical action, was tested as a leader on the acrylic line. The smoke condensation was eliminated by enclosing the promoter bath in a fume hood built in-house.

While modifying the continuous acrylic line to circumvent the initial problems in its operation, static tests utilizing the system described for the rayon batch trials were attempted. The staple acrylic yarn based on P16-type Monsanto fiber was utilized (Tables 3 and 4). The yarns were hand-impregnated in the glyceroxide solution, washed, and mounted in the 12-inch split-tube furnace for pyrolysis.

Conditions simulating as closely as possible those planned for the continuous pyrolysis line were employed (Figure 4). Variables screened included time of impregnation, oven atmospheres, and gas flow rates. None of the trials were successful, however, on the batch process, with breakages occurring in the 500°-800°C range. The yarns were extremely brittle, with

little strength remaining. Apparently, the differences between the batch simulation and the continuous process as described in the Monsanto patent were too severe to permit reaching the 1000°C temperature goal.[31]

After the hood and leader modifications were made in the continuous acrylic line, several runs were attempted using the P16 precursor. Breakage was a severe problem on the line, however, as detailed in Figure 4. The major problem was that too much tension developed in the long continuous line as the yarn passed around the numerous roller guides inherent in the various impregnation and wash baths. The tension was greater than the carbonized yarn could withstand, resulting in yarn failure. Also, the optimum flow rate of the yarn was detailed by the patent conditions to be different for impregnation and pyrolysis, based on the various equipment lengths.[31] Insufficient chemical and/or oxidative stabilization resulted from the single speed process, contributing to the breaks.

The continuous line of Figure 4 was thus separated after the drying oven to give two continuous processes, chemical impregnation and oxidative stabilization/carbonization, that comprised an overall semicontinuous process from precursor to carbon yarn. In the chemical impregnation processes, the yarn was prescoured with perchloroethylene, washed, impregnated in the glyceroxide bath, washed, dried, and collected behind the Servo motor/rubber roller apparatus that acted as a yarn drive. The impregnated yarn was then fed continuously into the 18-foot stabilization furnace, which was followed by the Lindberg oven at 1000°C. The Servo motor/rubber roller apparatus was also used as a yarn drive in the pyrolysis section, with the carbonized yarn collected behind the rubber rollers.

A single run was made with the P16 staple acrylic yarn on the semicontinuous process using the Owens-Corning glass yarn as a leader before the project was terminated. The yarn was manipulated through the continuous impregnation line at a speed that allowed 2.5 min. residence time in the glyceroxide bath, which was held at 190°C at a concentration of 0.02 meq/g of solution (Appendix B).[31] The impregnated yarn was yellow-orange in color after drying. The yarn was then continuously pulled (1.5 in/min.) behind the glass leader in a separate operation into the 18-foot furnace at 175°C and exited at 300°C, all under static air conditions. The yarn then entered the Lindberg carbonization oven directly at 1000°C, and was collected behind the Servo motor/roller system.

The carbonized acrylic yarn possessed good visual properties, being a greyish-black in color and showing excellent flexibility. The two plies of the yarn (Table 4) were clearly discernable, and the staple nature of the carbonized yarn was evident by the short carbon fibers protruding from the yarn sufrace to give a "hairy" appearance. The yarn appeared to be encouragingly strong in hand-breaks, and was qualitatively similar to samples of the carbonized yarns from the Avtex rayon trials. Due to termination of the project, no quantitative measurements of the yarn's mechanical, sorptive, or SEM properties were obtained.

CONCLUSIONS

Enka Supreme Cordenka Rayon Precursor

Several conclusions were drawn from the research conducted on the Enka Supreme Cordenka Rayon tire cord yarn, based on the pyrolysis runs detailed in Appendix C:

1. Several conclusions paralleled those reported in the literature concerning continuous pyrolysis of other rayon precursors:[12,13]
   a. Counterflowing the atmospheric gases in the direction of the yarn flow was preferred over concurrent flow.
   b. Although the mechanism of cellulose degradation has been reported to be the same under either N_2 or air,[2] heating in the presence of air in the low-temperature stages of the process appeared to give more beneficial stabilization conditioning for carbonization.
   c. The "path of least resistance" was necessary to process the brittle yarn, with a straight flow from drying oven to wind-up in Figure 1 preferred. The only tension necessary was that inherent in passage around the rollers in the various impregnation and wash baths.
   d. Fairly sophisticated temperature control was necessary in the various ovens, as the crucial temperature ranges for the predominanting degradation reactions were narrow.
   e. A brief wash immediately after the promoter impregnation bath was necessary to remove the high concentration of surface chemicals that promote interyarn fusion.
2. A brisk air flow was necessary through the drying oven to prevent water in the hot saturated air from condensing in the exit end of the tube and rewetting the yarn.
3. Perchloroethylene more effectively removed spin oils and other impurities than did ethanol.
4. The wind-up at the termination of the pyrolysis line had to be as simple as possible, with the yarn carried through no low-angle

bends or severe mechanical stress. A motor/reducer system that gave a dependable, constant low level winder speed was necessary.

5. Glass yarn continuous-filament leader produced by Owens-Corning at 11.2 gpd breaking strength/1207 denier worked extremely well as a leader for the rayon yarn, allowing more rapid heating of the ovens at start-up. Also, when breaks occurred, the hot ovens could be restrung with the glass leader yarn <u>without cooling</u>, with the exception that Oven IV's temperature had to be below 600°C to meet the yarn's thermal limitations. Without the glass leader, restringing with the rayon would have been impossible without cooling.
6. Experiments in which the carbonization promoter bath was bypassed and pure N_2 or air/N_2 mixtures were utilized in the pyrolysis ovens gave the best processibility obtainable with the Enka precursor, resulting in flexible yarns (Runs 73-78 and 86-92, Appendix C). Tarring was excessive, however, resulting in low carbon yields, weak yarns, and plugged tubes, and thus the non-promoter technique was concluded to be unfeasible based on the project's objectives.
7. The Supreme Cordenka yarn, due to no apparent defect in the pyrolysis process either chemical or mechanical, had a marked tendency to develop "hot spots" and to suddenly break during continuous carbonization about 700°C.

Due to the above conclusions, as well as information supplied by American Enka researchers on attempted continuous pyrolysis of similar "off-the shelf" tire cord yarns, the overall conclusion of this phase of the research was that the Enka Glanzstoff Supreme Cordenka rayon tire cord yarn specified in Contract No. DAAG17-76-C-0092 was not a feasible precursor candidate. In Section F, the contract had reported that the carbonized yarn supplied earlier to Natick by the 3M Company had been based on a "filament viscose, tire cord grade, in the style 600 series manufactured by American Enka Company". 3M Company had stated that the viscose yarn they were using as a precursor was no longer being manufactured. Conversations with Enka officials revealed that Style 600 series yarns had been very different in

nature from the Supreme Cordenka yarn. The Style 600 series was based on a textile-type viscose that was manufactured in a pot-spinning operation, and was thoroughly bleached and cleaned in a separate, individual operation. Thus, practically all residual chemicals such as zinc salts, sulfate salts, amines, etc., that had been introduced into the filaments during processing were removed. This fact correlates with the statement by the 3M researchers in example 3 of the relevant patent that "the starting yarn (in the 3M continuous pyrolysis experiments) was in a clean state and hence needed no scouring".[13] By contrast, the Supreme Cordenka yarn, an industrial-type cord, was continuously spun, washed, and dried with no bleaching involved. A major portion of the extraneous chemicals, therefore, were "locked" into the Cordenka yarn during processing and were not removed. Scouring with perchloroethylene partially removed the impurities, but not completely enough to avoid localized high concentrations, and thus sites were available for "hot spots" to develop on pyrolysis. Other critical faults with the Cordenka yarn in relation to good pyrolysis behavior were detailed earlier in this report.

Avtex Rayon Precursor

The conclusions from the Avtex rayon precursor research, detailed in Appendix D, were as follows:

1. The Avtex precursor yarn, designed and spun specifically for good carbonization behavior, possessed mechanical properties compatible with those specified in the project contract except for strength. The Avtex precursor yarn had a breaking strength of 3.1 gpd in Georgia Tech tests (Table 2), which was only 62% of the measured strength of the Enka Supreme Cordenka precursor yarn. The resulting yarn strengths of the carbonized Avtex material were low, corresponding to the rule that a 60% drop in strength on carbonization of rayon at a maximum temperature of 1000°C is normal.[4] Higher pyrolysis temperatures would result in regaining a portion of the tenacity by increasing the carbon crystallinity; such an increase in crystallinity, however, would result in a lower density of voids (less available surface area) due to the tighter packing, and would thus be detrimental to high sorptivity. Realistically, a tenacity range of 1.5-2.0 gpd for carbon yarns produced from the Avtex precursor at a

maximum temperature of $1000^{o}C$ is the optimum that can be obtained from a technical viewpoint.

2. The yarn exhibited extremely good pyrolysis behavior on the final version of the pyrolysis line (Figure 1), with continuous runs of sufficient length to adequately demonstrate the feasibility of the process (Runs 76 and 80, Appendix D). The ease of pyrolysis of the Avtex precursor using the same process that had proven unsuccessful with the Enka Supreme Cordenka tire cord confirmed the conclusion that the yarn breakage of the Supreme Cordenka was due to the chemical nature of the yarn, not the process as developed.
3. Conclusions 1-5 in the previous section applied to the Avtex precursor as well as the Enka Cordenka. No attempt was made with the Avtex precursor to bypass the carbonization promoter bath due to the low char:volatiles ratio observed in the Cordenka bypass experiments.
4. Sorptive tests on the carbonized yarns in which either pure N_2 or decomposition gases/static air was utilized in the 1000°C oven revealed that the activation was minimal, running 6.5-9.5% by weight increase in CCl_4 vapor (Table 7). The level of activation achieved was thus far below that specified by the contract (80% by weight), and thus it was concluded that atmospheres of higher oxidative capabilities than incorporated in the research were required with the Avtex-based yarn.
5. The breaking strength of all the carbonized yarns based on the Avtex rayon were poor in relation to the estimated maximum attainable tenacity of 1.5 - 2.0 gpd, ranging instead from 0.17 gpd - 0.39 gpd (Tables 6 and 8.). A plausible explanation for the low strengths were lengthwise slits observed in a majority of those filaments tested due to incomplete promoter penetration to the center of the filament diameter, producing in effect "hollow" carbon fibers.

The outer sheath thus remained the only load-bearing component of the carbonized filaments. Optimization of the yarn strength through heating of the impregnation bath to promote diffusion and to eliminate the hollow fiber formation, as well as introduction of a washing step to remove chemical deposits, offered some encouragement (Runs 51-81, Appendix D), but termination of the project prevented full development of the strength.

6. Scanning electron microscopy revealed valuable information on the carbonized yarn in addition to the hollow filament problem:

a. The yarns had well-defined surface integrity, with little visible fusion between filaments when the short aqueous rinse was placed after the promoter bath. Conversion to carbon was thus facile with the Avtex precursor.

b. The needle crystal nature of the chemical growth on the unwashed yarn surface indicated that the impregnation chemicals (or their degradation products) were subliming and locking into crystal growth at the surface. SEM/X-ray elemental analysis revealed that phosphorous was the major chemical element in the crystals, with practically no sodium present (Figure 11). Detailed analysis of the crystals was not possible, however, as potential lighter elements such as carbon, oxygen, nitrogen, and boron could not be detected by the instrument. The lack of sodium in the crystals indicated, however, that the material consisted of a phosphorous-based degradation product of NaH_2PO_4. Incorporation of the phosphorous with degradation products of [illegible]her H_3BO_3, the rayon, or N_2 was not discounted by [illegible] analysis.

c. Visual differences between yarns pyrolyzed at 1000°C under N_2, static air, or N_2/CO_2 mixtures were minimal, with no catastrophic surface etching resulting from introduction of the oxidizing atmospheres. Surface "bubbles" were observed on some of the CO_2-treated yarns by SEM, indicating that an upper limit of the N_2:CO_2 ratio (4:1) was

being reached without catastrophic failure. Hollow filaments were present in all of the carbonized yarns, regardless of atmosphere, in the absence of impregnation bath heating, and thus the problem was independent of the gases utilized.

7. Heating of the carbonization promoter bath presented a major processing problem due to the high salt concentration (Runs 51-62, Appendix D). The bath had to agitate fairly rapidly to prevent localized superheating and resultant decomposition/precipitation of the salts; however, rapid agitation tended to tangle the single yarn as it passed through the bath, resulting in snags and tension-related breaks. The initial water rinse was also introduced during Runs 54-62, and the actual causes of the breaks during these runs were not attributed solely to either bath heating or washing. No attempts were made to heat the bath after the improvements were made in the rinsing operation (Runs 76-81, Appendix D) due to the project's termination.
8. Washing of the carbon filaments on a continuous basis was found to be an extremely sensitive and difficult operation. Sufficient washing was required to completely remove the chemical deposits; too strenuous a washing action, however, fractured the brittle carbon filaments and created too much tension along the line (Runs 54-76, Appendix D). Although progress was made in maintaining processibility by reverting to a milder cascade wash system (Runs 76, 80-81), an optimum system to maximize <u>both</u> processibility and chemical removal was not attained before termination of the project.
9. Traverse winding of the Avtex-based carbon yarn on packages, using a modified pigtail guide on the traveler and a "straight-line" flow through the pyrolysis sequence, was deemed feasible by the research. Best results were realized by first obtaining processibility through the pyrolysis sequence without traverse, and then carefully incorporating the traverse while the line was running. Care had to be taken, however, to avoid sharp curvature of the yarn after carbonization, as well as sudden voltage fluctuations of the winder motor due to the weak nature

of the fiber. Either caused excessive breakage of the yarn.

The overall conclusion on the Avtex rayon was that the fiber demonstrated excellent potential as a continuously-pyrolyzed, sorptive carbon yarn precursor in the research. Problems such as level of sorptivity, hollow filament formation, and chemical deposition were not considered insurmountable based on the investigation, and indeed considerable progress was made in solving these problems prior to termination of the project (Appendix D). The initial strength of the precursor, however, dictated that a lower theoretical maximum tenacity for the carbon yarn (1.5-2.0 gpd) than had been specified in the contract (2.7 gpd) was likely in the pyrolysis temperature range of 1000°C. Such a low tenacity may or may not hamper further textile operations to be conducted on the carbonized yarns, such as coverage of the carbon yarns with more sorptive, traditional textile materials via braiding or weaving of the yarns into carbon fabrics.

Due to the time and effort spent on the unsuccessful Enka Cordenka precursor trials, insufficient time remained to fully optimize the Avtex system in the reported project. The encouraging results obtained in the Avtex trials, however, warranted future research efforts to realize the full potential of the precursor.

Static Tests on Rayon Precursor

None of the static tests on the Enka precursor with alternate promoter formulations indicated marked potential as a replacement for the 3M formulation.[13] In addition to the overall problem with the chemical nature of the Enka Supreme Cordenka detailed in this report, several additional factors surfaced in the static experiments:

1. It was impossible to simulate exactly on a batch basis the conditions attained on a continuous line such as that detailed in Figure 1. Thus only an approximation of the yarn's behavior on a continuous line was sought in the batch experiments.
2. The availability of new flame-retardant formulations that gave high char:volatiles ratios with cellulose was poor. The phosphoramide-based retardants possessed potential as carbonization promoter candidates in the static tests while simultaneously avoiding existing patents, as no sorptive carbon fibers produced with a phosphoramide had been claimed in the literature to the

Investigator's knowledge. From the research results, however, the comparison of Monsanto's MCC-100 and MCC-300 formulations with the 3M formulation[13] was not encouraging on the batch system (Appendix E).

The overall conclusion from the static tests was that, due to commercial unavailability of the phosphoramide-based flame retardant formulations and their comparatively poor performance in batch carbonization, a completely inorganic-salt based formulation was required to reach high char:volatiles ratios. The relevant literature supported this conclusion.[13-16] Due to the project's limitations, no attempt was made to derive a novel inorganic-salt based formulation and to screen the promoter on the static line.

Acrylic Yarn Precursor

Construction of an adequate continuous pyrolysis line for staple acrylic yarns was extremely difficult due to the inherent weakness of the precursor (Tables 3 and 4) and the lengthy preoxidation times required to fully stabilize the yarn in preparation for 1000°C exposure. Although the research was limited in the acrylic yarn line due to the emphasis of the contract on the rayon precursors, several important conclusions were drawn:

1. The Monsanto P16 acrylic staple yarn, available commercially in large supply (Table 4), demonstrated excellent potential as a continuously processed carbon yarn precursor.
2. Static bath evaluation of the acrylic precursors was deemed unfeasible due to the inability to closely correlate the batch conditions with the required continuous conditions.[31]
3. Sodium glyceroxide in glycerine, applied under the conditions reported by Menikheim[31], sufficiently promoted rapid and thorough oxidative stabilization such that continuous pyrolysis of the acrylic yarn was feasible. The impregnation treatment allowed the yarn to pass from 300-325°C to 1000°C without intermediate thermal staging.
4. Static air in the preoxidation phase of the process (200-300°C), in conjunction with nitrogen in the carbonization oven (1000°C), were adequate atmospheres for pyrolysis of the glyceroxide-

treated yarn. No attempt was made to incorporate oxidizing gases such as CO_2 or static air in the 1000°C oven.

5. A semicontinuous process, in which the line shown in Figure 4 was separated at the drying oven, was found to facilitate processing due to lower tension and optimized impregnation/pyrolysis yarn speeds. Sufficient experimentation was not accomplished, however, to completely eliminate the possibility of a fully continuous staple acrylic carbonization process.
6. The carbonized yarn produced on the semicontinuous process possessed good qualitative visual and mechanical properties. No quantitative data was collected, however.

The overall conclusion on the P16 staple acrylic yarn research was that the possibility of replacing rayon filament yarn with staple acrylic yarn as a sorptive carbon fiber precursor was not eliminated. The fact that the P16 staple yarn could be carbonized in a continuous fashion without excessive breaks was in itself significant, indicating excellent potential. Optimal sorptive and mechanical properties of the carbonized yarns based on the P16 precursor must be determined, however, before a final conclusion can be reached on the overall potential of the yarn as an alternative to the Avtex rayon. Termination of the reported project prevented the optimization and subsequent comparison.

RECOMMENDATIONS

Enka Supreme Cordenka Rayon Precursor

The research conclusively demonstrated that the chemical and physical nature of the rayon yarn, Enka Glanzstoff Supreme Cordenka tire cord, prevented its use as a suitable precursor for continuous production of a sorptive carbon fiber. Based on the research and the comments offered by American Enka personnel detailed herein, the Investigator thus recommends that no further research be directed toward evaluation of the Enka Cordenka as a carbon fiber precursor. It is unlikely that any "off-the-shelf" rayon tire cord yarn will perform adequately as a carbon fiber precursor, as the characteristics are similar to the Supreme Cordenka in order to optimize tire cord performance.

Avtex Rayon Precursor

The Avtex rayon precursor, designed and spun specifically for good carbonization characteristics, performed adequately as a continuous carbon fiber precursor. Further research is recommended to fully optimize the mechanical and sorptive properties of the carbon yarns from the Avtex precursor. Specifically, further research is needed to coordinate the heating of the carbonization promoter bath to eliminate hollow filaments with an adequate afterwash operation to fully remove all chemical deposits from the carbonized yarns. Different oxidizing atmospheres, to include complex gaseous mixtures[14] and steam[15] at 1000°C should be screened to define an optimum activation system to reach the goal of 80% by weight of CCl_4 vapor adsorption while not destroying the yarn's mechanical properties.

Static Tests on Rayon Precursor

New inorganic-based formulations should be screened as carbonization promoters with the Avtex rayon precursor on the static system. Several formulations have been reported to give percentage chars of greater than 50% as flame retardants on cellulose fabrics, but have not been exploited in the literature to facilitate sorptive carbon fiber production, e.g., tetrakis (hydroxymethyl) phosphonium hydroxide (THPOH).[5] Present technology advancements, such as polyphosphazene-based flame retardant finishes,[32] should also be screened as carbonization promoters for the Avtex precursor

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on the static system. Recent patents detailing different formulations and activation systems should also be screened.[14-16] Any tests conducted on static systems should be considered as simply rough screening investigations for the continuous line, however, due to the difficulty in simulating the continuous conditions exactly on a batch basis.

Acrylic Yarn Precursor

Although experimentation on the acrylic precursor was limited on the reported project, the encouraging results on the Monsanto P16 staple acrylic yarn warrants further investigation. Initially, the mechanical and sorptive properties of the carbonized yarn obtained in the developed semi-continuous system should be quantified.[31] Once quantified, the properties should be optimized by assessing such variables as temperatures of glyceroxide impregnation, dwell times, process speeds, etc. Additional research directed toward development of a fully-continuous operation should also be conducted. Finally, other commercially-available staple acrylic yarns, such as those detailed in Table 3, should be substituted for the P16 precursor on the optimized system to compare performances and properties.

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APPENDICES

APPENDIX A. CALCULATIONS FOR PREPARATION OF RAYON CARBONIZATION PROMOTER BATH[13]

Desired: 10ℓ of final solution

Assume: density ≈1g/cm^3 ≈1g/ml

20% w/w NaH_2PO_4 $\rightleftarrows$ 2.0×10^3g in 10ℓ (10^4g) of bath

4% w/w H_3BO_3 $\rightleftarrows$ 4.0×10^2g in 10ℓ (10^4g) of bath

Procedure:
1. Place 9.5ℓ of distilled water in a container.
2. Gradually stir in 2000g of NaH_2PO_4 (Fisher).
3. Gradually stir in 400g of H_3BO_3 (Fisher).

Final Bath Weight: 11900 g

Final % w/w, NaH_2PO_4: 16.8%

Final % w/w, H_3BO_3: 3.4%

APPENDIX B. CALCULATIONS FOR PREPARATION OF THE SODIUM GLYCEROXIDE IMPREGNATION BATH FOR THE ACRYLIC LINE[31]

Basis: 0.02 meq/g of solution, 1000 ml of volume

0.02 meq/g solution $\Rightarrow$ 2×10^{-5} eq/g soln.

Density of glycerine = 1.261 g/ml @ 20°C $\Rightarrow$ 1000 ml = 1.261×10^{3}g

3 NaOH + 1 Glycerine $\rightarrow$ totally alkoxylated glycerine

$\Rightarrow$ 1eq NaOH $\equiv$ 3 moles NaOH per mole of glycerine based on this reaction

$\Rightarrow$ 2×10^{-5} eq/g soln. $\equiv$ 6×10^{-5} moles/g soln.

MW_{NaOH} = 40.02 g/mole

$\Rightarrow$ (6×10^{-5} moles/g soln.)(4.002×10^{1} g/mole)

= 2.40×10^{-3}g NaOH/g soln.

Assume, due to dilute nature of solution, that:

solution weight $\approx$ glycerine weight

$$\Rightarrow \frac{2.40 \times 10^{-3}\text{g of NaOH}}{1 \text{ g soln.}} = \frac{X}{1.261 \times 10^{3}\text{g soln.}}$$

X = 3.03 g of NaOH/liter of glycerine

For other concentrations:[31]

Conc. (meq/g of soln.)	Amt. NaOH/ℓ of soln. (g)
0.02	3.03
0.04	6.06
0.05	7.58
0.06	9.09

APPENDIX C. RESULTS OF ENKA SUPREME CORDENKA RAYON PYROLYSIS RUNS

	Oven I			Oven II			Oven III						
Run No.	Max. Temp. (°C)	Gas	Flow (scfh)	Max. Temp. (°C)	Gas	Flow (scfh)	Max. Temp. (°C)	Gas	Flow (scfh)	Max. Temp. (°C)	Gas	Flow (scfh)	Comments
1[a]	210 (Break)	Air	Static	-	-	-	-	-	-				
2[a]	220 (Break)	N_2	6	-	-	-	-	-	-				
3[a]	220 (Break)	N_2	12	-	-	-	-	-	-				
4	210 (Break)	N_2	18	250	N_2	9	300 (Break)	CO_2 N_2	2 6				
5	225	N_2 Air	18 Low[b]	270	N_2	9	300 (Break)	CO_2 N_2	2 6				
6	228	N_2 Air	18 Low[b]	270	N_2	9	290 (Break)	CO_2 N_2	5 9				
7	218 (Break)	N_2 Air	6 Low[b]	-	-	-	-	-	-				
8	218 (Break)	N_2	6	-	-	-	-	-	-				
9	221	N_2	12	295	N_2	6	395 (Break)	N_2	6				
10	208 (Break)	N_2	12	-	-	-	-	-	-				
11	218 (Break)	N_2	12	-	-	-	-	-	-				
12	220 (Break)	N_2	12	-	-	-	-	-	-				

[a] Runs made without the ethanol prescour bath in the line.
[b] Supplied by a small air pump.

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APPENDIX C
(cont.)

Run No.	Oven I Max. Temp. (°C)	Oven I Gas	Oven I Flow (scfh)	Oven II Max. Temp. (°C)	Oven II Gas	Oven II Flow (scfh)	Oven III Max. Temp. (°C)	Oven III Gas	Oven III Flow (scfh)	Max. Temp. (°C)	Gas	Flow (scfh)	Comments
13	220 (Break)	N_2	12	-	-	-	-	-	-				
14	198 (Break)	N_2	12	-	-	-	-	-	-				
15	220 (Break)	N_2	8	-	-	-	-	-	-				
16	208 (Break)	N_2	8	280	N_2	8	-	-	-				
17	207	N_2	12	340 (Break)	N_2	8	280	N_2	8				
18	220 (Break)	N_2	12	-	-	-	-	-	-				
19	215	N_2	12	260 (Break)	N_2	9	-	-	-				
20	215	N_2	8	140 (Break)	N_2	12	-	-	-				
21	215	N_2	12	300	N_2	12	310 (Break)	N_2	9				Break at godet
22	215	N_2	18	280 (Break)	N_2	12	-	-	-				
23	215	N_2 Air	6 0.4	290 (Break)	N_2	12	-	-	-				
24	215	N_2 Air	6 0.4	160 (Break)	N_2	12	-	-	-				

APPENDIX C
(cont.)

Run No.	Oven I Max. Temp. (°C)	Oven I Gas	Oven I Flow (scfh)	Oven II Max. Temp. (°C)	Oven II Gas	Oven II Flow (scfh)	Oven III Max. Temp. (°C)	Oven III Gas	Oven III Flow (scfh)	Max. Temp. (°C)	Gas	Flow (scfh)	Comments
25	215	N_2 Air	6 0.4	280 (Break)	N_2	12	-	-	-				
26	215	N_2 Air	6 0.4	290	N_2	9	300 (Break)	N_2	9				Break at godet
27	215	N_2 Air	6 0.4	290 (Break)	N_2	9	-	-	-				
28	215	N_2 Air	6 0.4	240 (Break)	N_2	9							
29	215	N_2 Air	6 0.4	290 (Break)	N_2	9							
30	217 (Break)	N_2 Air	6	290	N_2	9							
31	215	N_2 Air	6 0.4	290	N_2	9	340 (Break)	N_2	9				Break at godet
32	216 (Break)	N_2 Air	6 0.4	290	N_2	9	-	-	-				
33	215	N_2	6	300 (Break)	N_2	9							
34	215	N_2	6	300 (Break)	N_2	9	240	N_2	9				
35	215	N_2	6	290	N_2	8	300 (Break)	N_2	7.5				Break at godet
36	215	N_2	6	290	N_2	8	395 (Break)	N_2	7.5				Break at godet

APPENDIX C
(cont.)

Run No.	Oven I Max. Temp. (°C)	Oven I Gas	Oven I Flow (scfh)	Oven II Max. Temp. (°C)	Oven II Gas	Oven II Flow (scfh)	Oven III Max. Temp. (°C)	Oven III Gas	Oven III Flow (scfh)	Max. Temp. (°C)	Gas	Flow (scfh)	Comments
37[c]	215 (Break)	Air N_2	2 6	-	-	-	-	-	-				Break; jumped off guides
38	215	Air N_2	2 6	310 (Break)	N_2	9	-	-	-				
39	215	Air N_2	2 6	290 (Break)	N_2	9	180	N_2	9				Break; slip on godet
40	215	Air N_2	2 6	290	N_2	9	340 (Break)	N_2	9				Break at godet
41	216	Air N_2	2 6	290	N_2	9	415 (Break)	N_2	9				
42	220 (Break)	Air N_2	2 6	-	-	-	-	-	-				
43	215	Air N_2	2 6	180 (Break)	N_2	9	-	-	-				
44	215	Air N_2	2 6	290	N_2	9	650 (Break)	N_2	9				Break; winder
45	215 (Break)	Air N_2	2 6	-	-	-	-	-	-				
46	215	Air N_2	2 6	280 (Break)	N_2	9	-	-	-				
47	215	N_2	8	295 (Break)	N_2	9	180	N_2	9				
48	215	N_2	8	300 (Break)	N_2	9	320	N_2	9				

[c] Impregnation bath changed and stainless steel clamps used to hold the submerged rollers in place.

APPENDIX C
(cont.)

Run No.	Dry Oven Max. Temp. (^oC)	Dry Oven Gas	Dry Oven Flow (scfh)	Oven I Max. Temp. (^oC)	Oven I Gas	Oven I Flow (scfh)	Oven II Max. Temp. (^oC)	Oven II Gas	Oven II Flow (scfh)	Oven III Max. Temp. (^oC)	Oven III Gas	Oven III Flow (scfh)	Comments
49	-	-	-	215	N_2	8	290	N_2	9	550 (Break)	N_2	9	Break at compensator
50	-	-	-	215	N_2	6	290	N_2	9	510 (Break)	N_2	9	Break at compensator
51	-	-	-	215	N_2	6	290	N_2	9	375 (Break)	N_2	9	
52	175	Air	6	215	N_2	6	290	N_2	9	300 (Break)	N_2	9	Break at winder pigtail
53	160	Air	6	215 (Break)	N_2 Air	6 2	-	-	-	-	-	-	Rough break
54	160	Air	6	215 (Break)	N_2 Air	6 2	-	-	-	-	-	-	Break at winder pigtail
55	160	Air	6	215	N_2 Air	6 2	290	N_2	9	175 (Break)	N_2	9	Pigtail break; converted to direct take-up
56	160	Air	6	215	N_2 Air	6 2	290	N_2	9	340 (Break)	N_2	9	In Oven III
57	160	Air	6	215	N_2 Air	6 2	290	N_2	9	300 (Break)	N_2	9	In Oven III; speed changed, 12 in/min to 8 in/min.
58	160	Air	6	215	N_2 Air	6 2	280	N_2	9	420 (Break)	N_2	9	In Oven III
59	160	Air	6	215	N_2 Air	6 2	280	N_2	9	420 (Break)	N_2	9	At last guide; Fiberglass yarn leader begun
60	160	Air	6	215	N_2 Air	6 2	250	N_2	9	500 (Break)	N_2	9	At glass/rayon knot, Oven III

APPENDIX C
(cont.)

Run No.	Dry Oven			Oven I			Oven II			Oven III			Comments
	Max. Temp. (°C)	Gas	Flow (scfh)	Max. Temp. (°C)	Gas	Flow (scfh)	Max. Temp. (°C)	Gas	Flow (scfh)	Max. Temp. (°C)	Gas	Flow (scfh)	
61	160	Air	6	215	N_2 Air	6 2	220 (Break)	N_2	9	-	-	-	Golden brown
62	160	Air	6	215	N_2 Air	6 2	265	N_2	9	270 (Break)	N_2	9	Yarn hung at feed
63	160	Air	6	215	N_2 Air	6 2	255	N_2	9	290 (Break)	N_2	9	In Oven II
64	160	Air	6	215	N_2 Air	6 2	260	N_2	9	260 (Break)	N_2	9	Roller tension too high (binding)
65	160	Air	6	215	N_2 Air	6 2	260	N_2	9	280 (Break)	N_2	9	In Oven III; pulley tension
66	160	Air	6	215	N_2 Air	6 2	260	N_2	9	300 (Break)	N_2	9	Changed EtOH to perch. 10 m/min.
67	160	Air	6	215	Air	Static	260	Air	Static	300 (Break)	N_2	6	At package
68	170	Air	6	220	Air	Static	260	Air	Static	450 (Break)	N_2	6	In Oven III
69	170	Air	6	225	N_2	6	260	N_2	6	450 (Break)	N_2	6	In Oven III
70	175	Air	6	215	N_2 Air	6 2	260	N_2	9	280 (Break)	N_2	9	In Oven III
71	175	Air	6	215	N_2 Air	6 2	300	N_2	9	700 (Break)	N_2	9	In Oven III
72	175	Air	6	215	N_2 Air	6 2	280	N_2	9	400 (Break)	N_2	9	In Oven III

APPENDIX C
(cont.)

Run No.	Dry Oven Max. Temp. (°C)	Dry Oven Gas	Dry Oven Flow (scfh)	Oven I Max. Temp. (°C)	Oven I Gas	Oven I Flow (scfh)	Oven II Max. Temp. (°C)	Oven II Gas	Oven II Flow (scfh)	Oven III Max. Temp. (°C)	Oven III Gas	Oven III Flow (scfh)	Comments
73*	175	N_2	10	220	N_2	4	260	N_2	9	400	N_2	9	No break; long period began, promoter bath by-pass (starred runs)
74*	175	N_2	10	230	N_2	4	300	N_2	9	450	N_2	9	Thin, more flexible long period, no break
75*	175	N_2	10	230	N_2	4	350	N_2	9	670 (Break)	N_2	9	Very thin
76*	175	N_2	8	230	N_2	8	310	N_2	9	650 (Break)	N_2	9	Entering Oven II
77*	175	N_2	6	230	N_2	6	290	N_2	9	460 (Break)	N_2	9	In Oven III
78*	175	N_2	8	230	N_2	8	260	N_2	9	500 (Break)	N_2	9	In Oven III
79	175	N_2 Air	5 1	230	N_2	8	270	N_2	9	320 (Break)	N_2	9	In Oven III; began using 50% less concentrated promoter bath
80	175	N_2 Air	5 1	230	N_2	8	270	N_2	6	360 (Break)	N_2	6	In Oven III
81	175	N_2 Air	5 1	230	N_2	8	300	N_2	6	370 (Break)	N_2	6	In Oven III; perchloroethylene bath added; full promoter bath
82	175	N_2 Air	5 1	230	N_2	8	300	N_2	6	400 (Break)	N_2	6	In Oven III; thin yarn
83	180	N_2 Air	5 1	230	N_2	8	260	N_2	6	400 (Break)	N_2	6	Entering Oven III
84	160	N_2 Air	5 1	230	N_2	8	260	N_2	6	500 (Break)	N_2	6	At glass/rayon knot entering Oven III

APPENDIX C
(cont.)

Run No.	Dry Oven Max. Temp. (^oC)	Dry Oven Gas	Dry Oven Flow (scfh)	Oven I Max. Temp. (^oC)	Oven I Gas	Oven I Flow (scfh)	Oven II Max. Temp. (^oC)	Oven II Gas	Oven II Flow (scfh)	Oven III Max. Temp. (^oC)	Oven III Gas	Oven III Flow (scfh)	Comments
85	160	N_2 Air	5 1	230	N_2	8	260	N_2	6	450 (Break)	N_2	6	At glass/rayon knot entering Oven III
86*	160	N_2 Air	5 1	250	N_2 Air	8 4	310	N_2	8	500 (Break)	N_2	8	By-passed promoter bath; thin
87*	160	Air	6	250	N_2 Air	2 4	350	N_2	8	850 (Break)	N_2	8	By-passed promoter bath; 4-hour run; thin, fairly flexible
88*	250	Air N_2	4 2	300	N_2	8	560	N_2	8	-	-	-	Break; Oven III after 2 hours; no promoter
89*	250	Air N_2	4 2	350	N_2	8	840	N_2	8	-	-	-	Oven II break; residue build-up; no promoter
90*	250	Air N_2	4 2	270	N_2	9	600	N_2	9	-	-	-	Oven III break; excessive smoking, tar formation; no promoter
91*	250	Air N_2	4 2	350	N_2	9	570	N_2	9	-	-	-	Break entering Oven III; tar build-up interference; no promoter
92	250	Air N_2	5 3	350	N_2	5	750	N_2	5	-	-	-	Reintroduced promoter bath; break at package after 2 hours
93	250	Air N_2	4 3	350	N_2	5	700	N_2	7	-	-	-	Break at package
94	250	Air N_2	5 3	350	N_2	5	560	N_2	5	-	-	-	Break at package; 8 in/min rate
95	250	Air N_2	5 3	350	N_2	5	450	N_2	5	-	-	-	Break at package; 14 in/min rate
96	250	Air N_2	5 3	350	N_2	10	500	N_2	10	-	-	-	Break at package; 10 in/min rate

APPENDIX C
(cont.)

Run No.	Oven I Max. Temp. (°C)	Oven I Gas	Oven I Flow (scfh)	Oven II Max. Temp. (°C)	Oven II Gas	Oven II Flow (scfh)	Oven III Max. Temp. (°C)	Oven III Gas	Oven III Flow (scfh)	Oven IV Max. Temp. (°C)	Oven IV Gas	Oven IV Flow (scfh)	Comments
97	250	Air N_2	3 3	350	N_2	5	630	N_2	10	-	-	-	Break at Oven III after 3 hours
98	250	Air N_2	3 3	350	N_2	5	600	N_2	10	-	-	-	Break at Oven III
99	250	Air N_2	3 3	350	N_2	5	600	N_2	10	-	-	-	Break at Oven III
100	250	Air N_2	3 3	350	N_2	7	580	N_2	7	-	-	-	Break at package
101	250	Air N_2	3 3	350	N_2	5	400	N_2	10	-	-	-	Break at Oven III; inserted Oven IV in line

APPENDIX D. RESULTS OF AVTEX SPECIALTY RAYON PRECURSOR RUNS*

Run No.	Oven I Max. Temp. (°C)	Oven I Gas	Oven I Flow (scfh)	Oven II Max. Temp. (°C)	Oven II Gas	Oven II Flow (scfh)	Oven III Max. Temp. (°C)	Oven III Gas	Oven III Flow (scfh)	Oven IV Max. Temp. (°C)	Oven IV Gas	Oven IV Flow (scfh)	Comments
1	250	Air N_2	3 3	350	N_2	5	400	N_2	10	800	N_2	10	Break, Oven IV after 4 hrs; used promoter bath
2	250	Air N_2	2 6	350	N_2	5	600	N_2	10	850	N_2	10	Break at Oven IV; stuck on sublimed salt build-up; 18 in/min. rate; several hrs; yarn flexible
3	250	Air N_2	2 6	350	N_2	5	600	N_2	10	500	N_2	10	Break at package
4	250	Air N_2	2 6	350	N_2	5	600	N_2	10	650	N_2	10	Break at Oven II; hung on entrance; yarn flexible
5	250	Air N_2	3 5	350	N_2	5	600	N_2	10	600	N_2	10	Break, Oven II
6	240	Air N_2	3 5	310	N_2	8	540	N_2	8	450	N_2	8	Break at package
7	240	Air N_2	3 5	330	N_2	5	600	N_2	8	600	N_2	10	Break at package
8	235	Air N_2	2 6	350	N_2	5	600	N_2	10	850	N_2	10	Break at Oven II
9	250	N_2 Air	4 2	350	N_2	5	600	N_2	10	760	N_2	15	Broke at package after 4 hours
10	250	N_2 Air	4 2	350	Air	2	600	N_2	5	400	N_2	10	Break at package
11	250	N_2 Air	4 3	350	N_2	5	600	N_2	10	500	N_2	15	Break at package
12	250	N_2 Air	4 2	350	N_2	5	600	N_2	10	620	N_2	15	Introduced H_2O rinse bath; break at package

*In all of the runs, the drying oven was kept at 160°C with 5-6 scfh of air.

APPENDIX D
(cont.)

Run No.	Oven I Max. Temp. (^oC)	Oven I Gas	Oven I Flow (scfh)	Oven II Max. Temp. (^oC)	Oven II Gas	Oven II Flow (scfh)	Oven III Max. Temp. (^oC)	Oven III Gas	Oven III Flow (scfh)	Oven IV Max. Temp. (^oC)	Oven IV Gas	Oven IV Flow (scfh)	Comments
13	250	N_2 Air	4 2	350	N_2	5	600	N_2	10	915	N_2	15	Break at package
14	250	N_2 Air	4 2	350	N_2	5	400	N_2	10	670	N_2	10	Break at package
15	240	Air	0	350	N_2	5	600	N_2	10	750	N_2	10	Break at package rate: 16-18 in/min.
16	250	N_2	4	350	N_2	5	600	N_2	10	1000	N_2	10	Rate: 12 in/min; ran continuously for 5 hours
17	250	N_2	4	350	N_2	10	600	N_2	10	700	N_2	10	Break at package
18	250	N_2	4	350	N_2	10	600	N_2	10	650	N_2	10	Break at package
19	250	N_2	4	350	N_2	10	600	N_2	10	675	N_2	10	Break at package
20	250	N_2	4	350	N_2	15	600	N_2	20	1000	N_2	20	Ran continuously for 6 hours
21a	250	N_2	4	350	N_2	6	600	N_2	10	1000	N_2	6	Ran continuously for approximately 10 hrs.
21b	250	N_2	4	350	N_2	6	600	Air	10	1000	Air	6	Break at package after approximately 5 hours.
22	250	N_2	4	350	N_2	10	600	N_2	10	800	N_2	10	Break at package
23	250	N_2	4	350	N_2	10	600	N_2	10	810	N_2	10	Break at Oven III
24	250	N_2	4	350	N_2	10	600	N_2	10	1000	N_2	10	Ran 1½ hr.w/only N_2 in Oven IV; bled in CO_2 & yarn broke at pack.

APPENDIX D
(cont.)

Run No.	Oven I Max. Temp. (°C)	Oven I Gas	Oven I Flow (scfh)	Oven II Max. Temp. (°C)	Oven II Gas	Oven II Flow (scfh)	Oven III Max. Temp. (°C)	Oven III Gas	Oven III Flow (scfh)	Oven IV Max. Temp. (°C)	Oven IV Gas	Oven IV Flow (scfh)	Comments
25	250	N_2	4	350	N_2	10	600	N_2	10	850	N_2	10	Break between Ovens III & IV; quartz tube broke
26	250	N_2	4	350	N_2	10	600	N_2	10	770	N_2	10	Break at Oven II; began altered system
27	250	N_2	4	350	N_2	10	600	N_2	10	800	N_2	10	Break at Oven III
28	250	N_2	4	350	N_2	10	600	N_2	10	710	N_2	10	Break at Oven III
29	250	N_2	4	350	N_2	10	600	N_2	10	760	N_2	10	Break between Ovens III & IV
30	250	N_2	4	350	N_2	10	600	N_2	10	800	N_2	10	Break at Oven III
31	250	N_2	4	350	N_2	10	600	N_2	10	800	N_2	10	Break at Oven IV
32	250	N_2	4	350	N_2	10	600	N_2	10	820	N_2	10	Break at Oven III
33	250	N_2	4	350	N_2	10	600	N_2	10	800	N_2	10	Break between Ovens II & III
34	140	N_2	4	350	N_2	6	600	N_2	6	600	N_2	6	Broke at package
35	250	N_2	4	350	N_2	10	600	N_2	10	780	N_2	10	Broke at Oven II
36	250	N_2	4	350	N_2	8	600	N_2	10	1000	N_2	10	Break at package

APPENDIX D
(cont.)

Run No.	Oven I Max. Temp. (°C)	Oven I Gas	Oven I Flow (scfh)	Oven II Max. Temp. (°C)	Oven II Gas	Oven II Flow (scfh)	Oven III Max. Temp. (°C)	Oven III Gas	Oven III Flow (scfh)	Oven IV Max. Temp. (°C)	Oven IV Gas	Oven IV Flow (scfh)	Comments
37	250	N_2	4	350	N_2	10	600	N_2	10	1000		10	Ran 5 hrs; some brittleness problems
38	250	N_2	4	350	N_2	8	600	N_2	8	1000	N_2	8	Broke in Oven IV
39	250	N_2	4	350	N_2	10	600	N_2	10	1000	N_2	10	Broke in Oven III
40	250	N_2	4	350	N_2	8	600	N_2	8	1000	N_2	8	Broke in Oven IV
41	250	N_2	4	350	N_2	8	600	N_2	8	1000	N_2	8	Ran 1 hour; broke in Oven III
42	250	N_2	4	350	N_2	8	600	N_2	8	1000	N_2	8	Ran ½ hour; broke in Oven II
43	250	N_2	4	350	N_2	5	600	N_2	5	1000	N_2	5	Ran 1 hour; broke in Oven II
44	250	N_2	4	350	N_2	5	600	N_2	5	1000	N_2 CO_2	5.5 0.5	Ran 1 hr. w/only N_2 in Oven IV;ran 1 hr.w/CO_2/N_2 mix;break, Oven IV
45a	250	N_2	4	350	N_2	5	600	N_2	5	1000	N_2 CO_2	5.5 0.5	Ran 4 hours; broke in Oven II
45b	250	N_2	4	350	N_2	5	600	N_2	5	1000	N_2 CO_2	5.25 0.75	Ran 2 hrs; broke in Oven II due to snag
45c	250	N_2	4	350	N_2	5	600	N_2	5	1000	N_2 CO_2	5.25 0.75	Ran 2 hours
45d	250	N_2	4	350	N_2	5	600	N_2	5	1000	N_2 CO_2	5 1.0	Ran 5 hours

APPENDIX D
(cont.)

Run No.	Oven I Max. Temp. (^oC)	Oven I Gas	Oven I Flow (scfh)	Oven II Max. Temp. (^oC)	Oven II Gas	Oven II Flow (scfh)	Oven III Max. Temp. (^oC)	Oven III Gas	Oven III Flow (scfh)	Oven IV Max. Temp. (^oC)	Oven IV Gas	Oven IV Flow (scfh)	Comments
45e	250	N_2	4	350	N_2	5	600	N_2	5	1000	N_2 CO_2	4.75 1.25	Broke immediately
46	250	N_2	5	350	N_2	5	600	N_2	5	600	N_2	5	Break in Oven III; traverse initiated
47	250	N_2	5	350	N_2	5	600	N_2	5	600	N_2	5	Break in Oven III
48	250	N_2	4	350	N_2	5	600	N_2	5	700	N_2	5	Break in Oven II due to threadline snag; traversing at package
49	250	N_2	4	350	N_2	5	600	N_2	5	900	N_2	5	Traversing; bled in CO_2 in Oven IV w/1:7 CO_2/N_2 ratio. Break after 2 hrs.due to threadline snag in bath
50	250	N_2	5	350	N_2	5	600	N_2	5	700	N_2	5	Oven III N_2 supply depleted; break at package
51	250	N_2	4	350	N_2	5	600	N_2	5	950	N_2	5	Carbonization bath heated to 65^oC; break in Oven II
52	250	N_2	4	350	N_2	5	600	N_2	5	920	N_2	5	Heated bath; break in Oven II
53	250	N_2	4	350	N_2	5	600	N_2	5	1000	N_2	5	Heated bath, ran ½ hour before break in Oven III
54	250	N_2	4	350	N_2	5	600	N_2	5	870	N_2	5	Inserted continuous water rinse; heated bath, break in Oven II
55	250	N_2	4	350	N_2	15	600	N_2	5	930	N_2	5	Heated bath, break in Oven III
56	250	N_2	4	350	N_2	15	600	N_2	15	860	N_2	5	Heated bath, break in Oven III

APPENDIX D
(cont.)

Run No.	Oven I Max. Temp. (°C)	Oven I Gas	Oven I Flow (scfh)	Oven II Max. Temp. (°C)	Oven II Gas	Oven II Flow (scfh)	Oven III Max. Temp. (°C)	Oven III Gas	Oven III Flow (scfh)	Oven IV Max. Temp. (°C)	Oven IV Gas	Oven IV Flow (scfh)	Comments
57	250	N_2	4	350	N_2	5	600	N_2	5	900	N_2	5	Heated bath, break in Oven III
58	250	N_2	4	350	N_2	5	600	N_2	5	900	N_2	5	Heated bath, break in Oven III
59	250	N_2	4	350	N_2	5	600	N_2	5	930	N_2	5	Heated bath, break in Oven II
60	250	N_2	5	350	N_2	5	600	N_2	5	900	N_2	5	Heated bath, break in Oven II
61	250	N_2	5	350	N_2	5	600	N_2	5	950	N_2	5	Heated bath, break in Oven II
62	250	N_2	5	350	N_2	5	600	N_2	5	920	N_2	5	Heated bath, no overfeed, break in Oven III
63	250	N_2	5	350	N_2	5	600	N_2	5	900	N_2	5	Carbonization bath at room temp. (20°C);break in Oven II
64	250	N_2	5	350	N_2	5	600	N_2	5	900	N_2	5	Unheated bath, break in Oven III
65	250	N_2	5	350	N_2	5	600	N_2	5	900	N_2	5	Unheated bath, break in Oven II
66	250	N_2	5	350	N_2	5	600	N_2	5	925	N_2	5	Unheated bath, break in Oven II
67	250	N_2	5	350	N_2	2.5	600	N_2	2.5	1000	N_2 CO_2	5 0.5	Unheated bath, ran 45 min.; break in Oven II
68	250	N_2	2	350	N_2	2.5	600	N_2	2.5	900	N_2	5	Unheated bath, break in Oven II

APPENDIX D
(cont.)

Run No.	Oven I Max. Temp. (^oC)	Oven I Gas	Oven I Flow (scfh)	Oven II Max. Temp. (^oC)	Oven II Gas	Oven II Flow (scfh)	Oven III Max. Temp. (^oC)	Oven III Gas	Oven III Flow (scfh)	Oven IV Max. Temp. (^oC)	Oven IV Gas	Oven IV Flow (scfh)	Comments
69	250	N_2	2	350	N_2	5	600	N_2	5	900	N_2	5	Unheated bath, break in Oven II
70	250	N_2	4	350	N_2	5	600	N_2	5	950	N_2	5	Unheated bath, break in Oven III
71	250	N_2	4	350	N_2	5	600	N_2	5	700	N_2	5	Broke in Oven II
72	250	N_2	2	350	N_2	5	600	N_2	5	700	N_2	5	Broke in Oven II
73	250	N_2	2	350	N_2	5	600	N_2	5	700	N_2	5	Broke in Oven III
74	250	N_2	2	350	N_2	5	600	N_2	5	700	N_2	5	Broke in Oven II
75	250	N_2	2	350	N_2	5	600	N_2	5	1000	N_2 CO_2	5 1	Ran well for 1 hour; broke upon addition of water cascade bath
76	250	N_2	2	350	N_2	5	600	N_2	5	1000	N_2 CO_2	5 1	Ran well for 7 hours; used modified cascade bath
77	250	N_2	2	350	N_2	5	600	N_2	5	800	N_2	5	Broke in Oven III
78	250	N_2	2	350	N_2	5	600	N_2	5	750	N_2	5	Broke in Oven III
79	250	N_2	2	350	N_2	5	600	N_2	5	700	N_2	5	Broke in Oven III
80	250	N_2	2	350	N_2	5	600	N_2	5	1000	N_2 CO_2	5 1	Ran well for 2 hrs.--broke after rod slipped in bath
81	250	N_2	2	350	N_2	5	600	N_2	5	1000	N_2 CO_2	5 1	Ran well for 6 hrs.

APPENDIX E. STATIC PYROLYSIS RESULTS ON ENKA SUPREME CORDENKA RAYON

Run No.	Impregnation Chemicals	Stage 1			Stage 2			Stage 3		
		Gas	Flow	Max. Temp.	Gas	Flow	Max. Temp.	Gas	Flow	Max. Temp.
1	MCC 100 NaH_2PO_4 H_3BO_3	N_2	12	140	N_2	12	210	N_2	8	300 (Break)
2	MCC 100	N_2	12	150	N_2	12	210	N_2	12	350 (Break)
3	MCC 100	N_2	12	150	N_2	12	210	N_2	12	290 (Break)
4	MCC 300	N_2	12	150	N_2	12	210	N_2	12	350 (Break)
5	50% strength[1] NaH_2PO_4/H_3BO_3	Air	2	215	N_2 Air	6 2	260	N_2	9	618 (Break)
6	MCC 300	Air	2	215	N_2 Air	6 2	260	N_2	9	212 (Break)
7	MCC 100	Air	2	215	N_2 Air	6 2	260	N_2	9	456 (Break)
8	MCC 300	Air	2	215	N_2 Air	6 2	260	N_2	9	495 (Break)
9	25% strength NaH_2PO_4/H_3BO_3	Air	2	215	N_2 Air	6 2	260	N_2	9	492 (Break)

APPENDIX E
(cont.)

Run No.	Impregnation Chemicals	Gas	Flow	Max. Temp.	Gas	Flow	Max. Temp.	Gas	Flow	Max. Temp.
10	25% strength NaH_2PO_4/H_3BO_3	Air	2	215	N_2 Air	6 2	260	N_2	9	679 (Break)
11	75% strength NaH_2PO_4/H_3BO_3	Air	2	215	N_2 Air	6 2	260	N_2	9	677 (Break)
12	50% strength NaH_2PO_4/H_3BO_3	Air	2	215	N_2 Air	6 2	260	N_2	9	733 (Break)

ABBREVIATIONS, ACRONYMS, AND SYMBOLS
(In order of appearance in text)

Item	Meaning
^oC	degrees Celcius
%	percent
CCl_4	carbon tetrachloride
gpd	grams per denier
NaH_2PO_4	monosodium phosphate
H_3BO_3	boric acid
H_2O	water
CO	carbon monoxide
CO_2	carbon dioxide
etc.	et cetera
HPGF	high performance graphite fibers
Z-twist	right-hand twist
^oF	degrees Farenheit
O_2	oxygen
HCl	hydrogen chloride
N_2	nitrogen
min	minutes
vol	volume
mg/g	milligrams/gram
cm^2	centimeters squared
ml	milliliters
m^2/g	meter squared/gram
C_6H_6	benzene
^ok	Kelvin
gpf	grams per filament
fil/yarn	filaments/yarn
TPI	turns per inch
lb	pound
% w/w	percent weight of solute per weight of solution
ℓ	liters
meq/g	milliequivalents/gram

ABBREVIATIONS, ACRONYMS, AND SYMBOLS
(cont.)

Item	Meaning
g/l	grams/liter
DIA	diameter
in./min.	inches/minute
OD	outside diameter
scfh	standard cubic feet per hour
max.	maximum
dpf	denier per filament
R.H.	relative humidity
Fil/yarn	number of filaments per yarn
HBO_2	dehydrated boric acid
SEM	scanning electron microscope or microscopy
soln.	solution